UNIWERSYTET ŚLĄSKI
W KATOWICACH

INSTYTUT FIZYKI
ZAKŁAD BIOFIZYKI I FIZYKI MOLEKULARNEJ

PRACA DOKTORSKA:

DYNAMICZNE I TERMODYNAMICZNE ASPEKTY PRZEJŚCIA SZKLISTEGO

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KATOWICE 2015

Chciałbym serdecznie podziękować

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za wskazanie interesującej tematyki,

cenne uwagi i wszechstronną pomoc.

Składam serdeczne podziękowania

za życzliwość, poświęcony czas

oraz ogromne wsparcie merytoryczne

Panu dr. Andrzejowi Grzybowskiemu.

Do powstania niniejszej rozprawy doktorskiej w znaczącym stopniu przyczyniło się stypendium, otrzymane przeze mnie w ramach programu „DoktoRIS – Program stypendialny na rzecz innowacyjnego Śląska" współfinansowanego przez Unię Europejską w ramach Europejskiego Funduszu Społecznego.

KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI
FUNDUSZ SPOŁECZNY

SPIS TREŚCI:

1. PUBLIKACJE NAUKOWE STANOWIĄCE PODSTAWĘ ROZPRAWY DOKTORSKIEJ

Niniejsza rozprawa doktorska pt. „Dynamiczne i termodynamiczne aspekty przejścia szklistego" stanowi zbiór czterech artykułów naukowych opublikowanych w recenzowanych czasopismach, znajdujących się na liście filadelfijskiej (A1-A4):

L.p.	Publikacja	str.	Aktualny „Impact Factor" czasopisma	Aktualna liczba punktów MNiSW czasopisma
A1.	K. Koperwas, A. Grzybowski, K. Grzybowska, Ż. Wojnarowska, J. Pionteck, A. P. Sokolov, M. Paluch, *„Pressure coefficient of the glass transitioin temperature in the thermodynamic sacling regime"* **Phys. Rev. E 86**, 041502 (2012)	23	2.288	35
A2.	K. Koperwas, A. Grzybowski, K. Grzybowska, Ż. Wojnarowska, M. Paluch, *„Effects of dynamic heterogeneity and density scaling of molecular dynamics on the relationship among thermodynamic coefficients at the glass transition"* **J. Chem. Phys. 143,** 024502 (2015)	30	2.952	35

A3.	K. Koperwas, A. Grzybowski, K. Grzybowska, Ż. Wojnarowska, M. Paluch, *„In search of correlation between the four-point measure of dynamic heterogeneity and other characteristics of the glass-forming liquids under high pressure”* **J. Non-Cryst. Sol. 407**, 196 (2015)	36	1.766	30
A4.	K. Koperwas, A. Grzybowski, S. N. Tripathy, E. Masiewicz, M. Paluch, *„Thermodynamic consequences of the kinetic nature of the glass transition”* **Sci. Rep. 5**, 17782 (2015)	46	5.578	40

Jestem również współautorem sześciu innych artykułów naukowych, które tematycznie są bardzo zbliżone do artykułów A1-A4, stanowiących niniejszą rozprawę doktorską:

B1. „*Effects of lowering temperature and raising pressure on the spatially heterogeneous dynamics of glass-forming van der Waals liquids*”, A. Grzybowski, K. Kolodziejczyk, K. Koperwas, K. Grzybowska, and M. Paluch, Phys. Rev. B 85, 220201 (2012),

B2. „*Scaling of volumetric data in model systems based on the Lennard-Jones potential*”, A. Grzybowski, K. Koperwas, and M. Paluch, Phys. Rev. E 86, 031501 (2012),

B3. „*Activation volume in the density scaling regime: Equation of state and its test by using experimental and simulation data*”, A. Grzybowski, K. Koperwas, A. Święty-Pośpiech, K. Grzybowska, M. Paluch, Phys. Rev. B 87, 054105 (2013),

B4. „*Effect of temperature and density fluctuations on the spatially heterogenous dynamics of glass-forming van der Waals liquids under high pressure*", K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, A.P. Sokolov, M. Paluch, Phys. Rev. Lett. 111, 125701 (2013),

B5. „*Spatially heterogeneous dynamics in the density scaling regime: time and length scales of molecular dynamics near the glass transition*", A. Grzybowski, K. Koperwas, K. Kołodziejczyk, K. Grzybowska, M. Paluch, J. Phys. Chem. Lett 4, 4273 (2013),

B6. „*Equation of state in the generalized density scaling regime studied from ambient to ultra-high pressure conditions*", A. Grzybowski, K. Koperwas, M. Paluch, J. Chem. Phys. 140, 044502 (2014).

2. OMÓWIENIE CELU NAUKOWEGO PRACY BADAWCZEJ

2.1. WSTĘP

Głównym celem przeprowadzonych badań, których wyniki przedstawione są w artykułach A1-A4, jest sformułowanie relacji opisującej współzależność pomiędzy wielkościami termodynamicznymi podczas przejścia szklistego. Motywacją dla podjętych starań jest brak eksperymentalnie potwierdzonej relacji pomiędzy wielkościami termodynamicznymi w przejściu szklistym.

Pomimo, iż intensywne badania procesu transformacji cieczy przechłodzonej do stanu szklistego prowadzone są od lat pięćdziesiątych poprzedniego stulecia, sformułowanie kompletnej teorii opisującej mechanizm przejścia szklistego jest wciąż jednym z najbardziej wymagających zadań współczesnej fizyki materii skondensowanej. Rozwiązanie powyższego problemu utrudnia fakt, że temperatura przejścia szklistego nie zależy wyłącznie od stanu termodynamicznego w jakim znajduje się układ, ale również od tempa z jakim dany układ został do powyższego stanu doprowadzony (tzn. od szybkości izobarycznego schładzania lub izotermicznej kompresji). W ciągu ponad 60 lat intensywnych badań nad procesem transformacji z metastabilnego stanu cieczy przechłodzonej do szkła zaproponowane zostały różne idee jego opisania.

2.1.1. TERMODYNACZNE ASPEKTY PRZEJŚCIA SZKLISTEGO

Jeden z pierwszych sposobów wyjaśnienia powyższego zjawiska opierał się na własnościach termodynamicznych przejścia szklistego. Niezaprzeczalnym jest, że podczas transformacji ciecz-szkło, energia swobodna Gibbsa oraz jej pierwsze pochodne (tzn. objętość v i entropia S) zmieniają się w sposób ciągły, podczas gdy jej drugie

pochodne, które są odzwierciedlone we współczynnikach termodynamicznych (np. rozszerzalności izobarycznej α_p , ściśliwości izotermicznej κ_T , izobarycznym C_p i izochorycznym C_v cieple właściwym) zmieniają się w sposób skokowy. Powyższej wskazane zachowanie wielkości termodynamicznych sugeruje, że przejście szkliste mogłoby być traktowane jako przejście fazowe drugiego rodzaju. Dlatego, w literaturze poświęconej przejściu szklistemu, wielokrotnie próbowano opisać wpływ ciśnienia na temperaturę przejścia szklistego, który jest w naturalny sposób określony poprzez tzw. ciśnieniowy współczynnik temperatury przejścia szklistego (dT_g / dp), za pomocą wzorów Ehrenfesta:

$$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_p} \quad \text{oraz} \tag{1a}$$

$$\frac{dT}{dp} = vT_g \frac{\Delta\alpha_p}{\Delta C_p}, \tag{1b}$$

gdzie Δ oznacza różnicę pomiędzy wartością odpowiedniego współczynnika mierzoną w cieczy i w szkle. Tym samym wynikająca z wzorów Ehrenfesta relacja Prigogine'a-Defaya,

$$\Pi = \frac{1}{vT_g} \frac{\Delta C_p \Delta\kappa_T}{\left(\Delta\alpha_p\right)^2} \equiv 1, \tag{2}$$

powinna być słuszna w przejściu szklistym[1,2,3]. Już pierwsze weryfikacje poprawności wzorów Ehrenfesta i relacji Prigogine'a-Defaya w przejściu szklistym wykazały ich znaczne niezgodności z wynikami analiz danych eksperymentalnych. Należy jednak podkreślić, że podczas przejścia fazowego drugiego rodzaju układ transformuje się z jednego stanu równowagowego do drugiego, podczas gdy w trakcie przejścia ciecz-szkło metastabilny stan równowagowy cieczy przechłodzonej przechodzi

do nierównowagowego stanu szklistego. Powyższe wyklucza traktowanie tego procesu jako przejścia fazowego drugiego rodzaju, a tym samym wyjaśnia udokumentowane nieprawdziwości wzorów Ehrenfesta oraz relacji Prigogine'a-Defaya. Niemniej jednak, z termodynamicznego punktu widzenia, różnice pomiędzy stanem równowagowym a nierównowagowym mogą zostać opisane za pomocą idei parametrów porządku, zaproponowanej przez Th. de Dondera i P. van Rysselberghe'a[4]. Zgodnie z nią, oba wyżej wymienione stany zależą nie tylko od wielkości termodynamicznych (np. temperatury i ciśnienia), ale również od szeregu strukturalnych parametrów porządku. Wykorzystując powyższy pomysł, F. Simon[5] opisał przejście szkliste jako proces, w którym układ zostaje „kinetycznie zamrożony", tzn. jego strukturalna reorganizacja (zmiana wartości parametrów porządku) nie podąża za dalszą zmianą wielkości termodynamicznych. Zakładając, że tylko jeden parametr porządku jest wystarczający do scharakteryzowania strukturalnych różnic pomiędzy cieczą a szkłem, R. O. Davis i G. O. Jones[6] wyprowadzili oba równania Ehrenfesta oraz relację Prigogine'a-Defaya. Od tej pory relacja Prigogine'a-Defaya stała się miarą skomplikowania układu mówiącą o stopniu w jakim system odbiega od jednoparametrowego opisu[7]. Należy jednak zauważyć, że opis przejścia szklistego w sposób zaproponowany przez F. Simona zakłada, że wartość parametrów porządku nie zależy od szybkości zmiany wielkości termodynamicznej (temperatury, ciśnienia). Założenie to nie jest prawdziwe dla gęstych układów, jakimi są ciecze przechłodzone w pobliżu T_g, w których zmiana wartości parametrów porządku nie nadąża za zamianami wielkości termodynamicznych. Takie zachowanie sugeruje, że skala czasowa zmian wielkości termodynamicznych staje się porównywalna z czasem relaksacji charakteryzującej system, τ_R, np. relaksacji strukturalnej (τ_α). W konsekwencji, wartość parametrów porządku różni się od swojej

wartości równowagowej[8]. Powyższe poddaje w wątpliwość zarówno zaproponowany termodynamiczny opis przejścia szklistego, jak również słuszność wzorów Ehrenfesta i relacji Prigogine'a-Defaya (nawet dla układów jednoparametrowych), a ponadto zwraca szczególną uwagę na kinetyczną naturę przejścia ciecz-szkło.

2.1.2. DYNAMICZNE ASPEKTY PRZEJŚCIA SZKLISTEGO

Liczne dotychczasowe badania fazy szklistej wykazały, że temperatura przejścia szklistego nie jest stała, a zależy od tempa doprowadzenia układu do punktu transformacji ciecz-szkło. Ponadto własności szkieł zmieniają się wraz z upływem czasu. Fakty te definitywnie wykluczają wyłącznie termodynamiczną naturę przejścia szklistego. Dlatego jest ono traktowane jako efekt kinetyczny. Warto zaznaczyć, że pierwsze próby opisania przejścia szklistego w powyższy sposób zostały podjęte już w 1949 roku niezależnie przez G. O. Jonesa[9] i G. M. Barteneva[10]. G. M. Bartenev dwa lata później zaproponował następującą relację $\left|\frac{dT}{dt}\tau_R\right|_{T_g} = const.$, wiążącą tempo doprowadzenia układu do przejścia szklistego (tempo chłodzenia dT/dt) z czasem charakterystycznej relaksacji układu[11]. Słuszność powyższej współzależności została potwierdzona dla wielu substancji[12, 13, 14] i uznana za ogólnie poprawną w przejściu szklistym[15, 16]. Zgodnie z nią, przy stałym tempie chłodzenia, wyłącznie czas charakterystycznej relaksacji układu definiuje punkt przejścia szklistego. Powyższe jest zgodne z eksperymentalnym sprawdzeniem rozważań dotyczących liczby Deborah'a zaproponowanej przez M. Hodge'a[17]. M. Hodge traktując relaksację strukturalną (τ_α) jako τ_R, wykazał, że człon $\tau_\alpha\Big|_{T_g}\frac{dT}{dt}$ jest w przybliżeniu równy iloczynowi $\ln 10\frac{T_g}{m_p}$

($m_p = \left(\frac{\partial \log \tau}{\partial T / T_g} \right)_p \Big|_{T=T_g}$ to kruchość izobaryczna), który z dobrym przybliżeniem jest stały, ponieważ wartości ilorazu T_g / m_p (otrzymana z analizy wyników pomiarów spektroskopii dielektrycznych różnych substancji) zmienia się bardzo nieznacznie wraz ze wzrostem ciśnienia. Znikoma zmiana T_g / m_p implikuje wzrost wartości $\tau_\alpha \big|_{T_g}$ tylko o kilka procent, podczas gdy ciśnienie rośnie od 0 do 200 lub nawet 300 MPa. Tym samym przejście szkliste jest definiowane (z bardzo dobrym przybliżeniem) poprzez konkretną i stałą wartość czasu relaksacji strukturalnej, $\tau_\alpha \big|_{T_g} = \tau_g$.

Prace badawcze, których wyniki przedstawione są w publikacjach A1-A4, bazują na definicji przejścia szklistego poprzez ustaloną wartość czasu relaksacji strukturalnej, τ_g. Zostały one ukierunkowane na wyprowadzanie formuły opisującej ciśnieniowy współczynnik temperatury przejścia szklistego, która byłaby alternatywą dla nieprawdziwych w przejściu szklistym wzorów Ehrenfesta. Ponadto celem badań było zaproponowanie współzależności pomiędzy wielkościami termodynamicznymi podczas przejścia ciecz-szkło, ekwiwalentnej do błędnej podczas tego procesu relacji Prigogine'a-Defaya.

3. OMÓWIENIE OSIĄGNIĘTYCH WYNIKÓW WRAZ Z ICH EWENTUALNYM WYKORZYSTANIEM

3.1. SKALOWANIE GĘSTOŚCIOWE

Jednym z rezultatów licznych badań relaksacji strukturalnej, zasługującym na szczególną uwagę, jest zaobserwowane dla ponad 100 różnych substancji (głównie cieczy van der Waalsa i polimerów) potęgowe skalowanie gęstościowe (termodynamiczne skalowanie). Zgodnie ze skalowaniem gęstościowym czasy relaksacji strukturalnej (lub segmentalnej w przypadku polimerów) zmierzone w różnych warunkach termodynamicznych, mogą zostać wykreślone na jednej wspólnej krzywej, opisanej równaniem skalowania $\tau_\alpha = f\left(T v^\gamma\right)$. Wykładnik skalujący γ jest stałą materiałową niezależną od warunków termodynamicznych. Ponadto, wykorzystując symulacje komputerowe dynamiki molekularnej, potwierdzono zaproponowane teoretyczne uzasadnienie skalowania gęstościowego wiążące γ z potencjałem międzymolekularnym. Wykazano, że uogólniony potencjał Lennarda-Jonesa opisujący oddziaływania van der Waalsa w gęstych układach, może być bardzo dobrze przybliżony przez efektywny, krótko-zasięgowy potencjał, $U_{eff}\left(r\right) = Ar^{-3\gamma} + B$, odpowiedzialny za skalowanie gęstościowe. Składa się on z dominującej części odzwierciedlającej oddziaływania odpychające „ $Ar^{-3\gamma}$ ” i stałego lub liniowego tła opisującego oddziaływania przyciągające „ B ”. Bezpośrednie połącznie potencjału międzymolekularnego z wykładnikiem skalującym sprawia, że skalowanie gęstościowe

jest niezwykle interesującą własnością relaksacji strukturalnej substancji formujących szkła.

Analiza wpływu ciśnienia na temperaturę przejścia szklistego cieczy przechłodzonych, w których zachodzi skalowanie gęstościowe, stanowi tematykę publikacji A1. W artykule, analizując dane wolumetryczne i relaksacyjne dla trzech substancji potwierdziłem, że przejście szkliste występuje w stałym czasie relaksacji oraz że skalowanie gęstościowe postaci $\tau_\alpha = f\left(T\upsilon^\gamma\right)$ jest słuszne dla badanych substancji. W publikacji zaproponowałem również nową relację opisującą ciśnieniowy współczynnik temperatury przejścia szklistego, $\frac{dT_g}{dp} = \frac{\gamma T_g \kappa_T}{1+\gamma T_g \alpha_p}$. Warto zaznaczyć, że wyprowadzony wzór jest bezpośrednio połączony z potencjałem międzymolekularnym poprzez wykładnik skalujący γ. Wykorzystując wartości wykładnika skalującego wyznaczone samodzielnie lub zaczerpnięte z danych literaturowych, z sukcesem sprawdziłem (dla dziesięciu typowych cieczy tworzących szkła) słuszność zaproponowanego wzoru na dT_g / dp. W artykule przeprowadziłem również dyskusję dotyczącą zachowania ciśnieniowego współczynnika temperatury przejścia szklistego dla modelowego układu twardych sfer. Układ ten opisywany jest poprzez potencjał, w którym wykładnik części odpychającej, a tym samym γ, dążą do nieskończoności. Dla tego rodzaju modelowych systemów objętość odgrywa główną rolę w dynamice molekularnej, a wkład pochodzący od fluktuacji temperatury jest znikomy. W tym przypadku wzór opisujący dT_g / dp okazał się identyczny z relacją uzyskaną również dla tego modelowego systemu przez niemieckiego naukowca J. W. P. Schmelzera[3]. Na przykładzie analizowanych substancji rzeczywistych wykazałem, że otrzymana

przez J. W. P. Schmelzera graniczna postać wzoru na dT_g / dp nie przewiduje poprawnych wartości ciśnieniowego współczynnika temperatury przejścia szklistego, ponieważ nie uwzględnia roli temperatury w dynamice molekularnej, a zatem również w przejściu szklistym.

3.2. DYNAMICZNA HETEROGENICZNOŚĆ

Jedną z fundamentalnych własności dynamiki molekularnej materiałów znajdujących się w pobliżu przejścia szklistego jest jej heterogeniczny charakter. Podczas ochładzania substancji (lub jej kompresji) odległości pomiędzy cząsteczkami maleją, a ich ruchy stają się zależne od siebie. Sprawia to, że wewnątrz cieczy przechłodzonych tworzą się regiony, w obrębie których przegrupowania molekuł mogą odbywać się wyłącznie w sposób kooperatywny, co jako pierwsi zasugerowali G. Adam i J. H. Gibbs już w 1965 roku[18]. Późniejsze badania wykazały, że rozmiary powyższych regionów nie są stałe w czasie i w przestrzeni, a dynamika cząsteczek należących do różnych obszarów kooperatywnego przegrupowania nie jest jednakowa. W konsekwencji prowadzi to do różnicowania dynamiki całego układu, która staje się heterogeniczna. W ostatnich latach do opisu dynamicznej heterogeniczności systemu została zaproponowana czteropunktowa czasowo-przestrzenna funkcja korelacji – dynamiczna podatność, $\chi_4(t)$. Amplituda piku $\chi_4(t)$, tzn. stopień dynamicznej heterogeniczności ($\chi_4^{\max}$), utożsamiana jest z rozmiarem regionów, wewnątrz których ruchy molekuł są zależne od siebie, a co za tym idzie, z ilością dynamicznie skorelowanych cząsteczek. Niestety bezpośrednie pomiary $\chi_4(t)$ nie są możliwe za pomocą standardowych metod spektroskopowych, ponieważ wymagają detekcji

nieliniowej podatności czwartego rzędu, co jest niezwykle trudnym zadaniem w układach znajdujących się w pobliżu przejścia ciecz-szkło. Z powyższego powodu zaproponowane przez L. Berthiera[19, 20] i jego współpracowników estymaty stopnia dynamicznej heterogeniczności, stały się niezwykle interesującą alternatywą. Zostały one uzyskane dzięki niebezpośredniej analizie stopnia dynamicznej heterogeniczności, bazującej na rozważaniach wpływu fluktuacji entalpii (H), gęstości (ρ) i temperatury na różnicowanie dynamiki.

Przedstawione w artykule A2 badania ciśnieniowego współczynnika temperatury przejścia szklistego, opierają się na zaproponowanej przez L. Berthiera wzajemnej relacji pomiędzy wkładami do stopnia dynamicznej heterogeniczności, $\chi_4^{\max} \approx \left(\chi_4^H\right)^{\max} \approx \left(\chi_4^T\right)^{\max} + \left(\chi_4^\rho\right)^{\max}$. Warto wspomnieć, że w publikacji B4, której jestem współautorem, została sprawdzona słuszność powyższej relacji w różnych warunkach termodynamicznych, także tych, które odpowiadają warunkom izochronicznym determinującym przejście szkliste, τ_g. W publikacji A2, rozważając relaksację strukturalną jako funkcję temperatury i ciśnienia, wyprowadziłem relację łączącą ciśnieniowy współczynnik temperatury przejścia szklistego i stopień dynamicznej heterogeniczności $\left(\frac{dT}{dp}\right)^2 \approx \frac{T\upsilon\kappa_T}{\Delta C_p}\left(\frac{\left(\chi_4^H\right)^{\max} - \left(\chi_4^T\right)^{\max}}{\left(\chi_4^H\right)^{\max}}\right)$. Następnie, wykorzystując jedną z konsekwencji skalowania gęstościowego, przekształciłem otrzymany wzór do następującej, wygodniejszej w użyciu postaci: $\frac{dT_g}{dp} \approx T_g \kappa_T \gamma \left(\frac{\Delta C_p}{\Delta C_\upsilon} + \gamma^2 \kappa_T T_g \rho \Delta C_p\right)^{-1/2}$.

Warto dodać, że do otrzymania wzoru na dT_g / dp przedstawionego w artykule A2 nie jest konieczne, aby wykładnik skalujący był stały w szerokim zakresie czasów relaksacji, lecz tylko, aby był niezmienniczy w warunkach izochronicznych, co w punkcie przejścia

szklistego, $\tau_g = f\left(T_g \upsilon_g^{\gamma}\right)$, odpowiada liniowej zależności $\log T_g$ od $\log \upsilon_g$. W konsekwencji należy podkreślić, że słuszność wyprowadzonego wzoru nie ogranicza się wyłącznie do substancji podlegających „standardowemu" skalowaniu gęstościowemu. Może być on zatem z powodzeniem zastosowanych dla cieczy, których molekuły wykazują tendencję do formowania wiązań wodorowych. Dla tych substancji postać równania skalującego, w której wykładnik skalujący zależy od czasu relaksacji, była sugerowana w literaturze. W omawianym artykule potwierdziłem słuszność wyprowadzonego wzoru na dT_g / dp dla trzynastu substancji należących do różnych grup materiałowych, w tym wspomnianych wyżej cieczy, w których występują wiązania wodorowe. Biorąc pod uwagę, że uzyskany w poprzednio omawianym artykule A1 wzór na dT_g / dp , może być również wyprowadzony wyłącznie w warunkach liniowej zależności $\log T_g\left(\log \upsilon_g\right)$, połączyłem obie otrzymane relacje i w konsekwencji uzyskałem następującą formułę: $\Pi_{GT} = \dfrac{\left(\dfrac{\Delta C_p}{\Delta C_\upsilon} + \gamma^2 \kappa_T T_g \rho \Delta C_p\right)^{1/2}}{1 + \gamma T_g \alpha_p} \approx 1$. Podobnie jak relacja Prigogine'a-Defaya opisuje ona współzależność pomiędzy wielkościami termodynamicznymi, w związku z czym może być jej odpowiednikiem dla przejścia ciecz-szkło. Należy podkreślić, że eksperymentalne wartości Π_{GT} okazały się zgodne z ich teoretycznymi oczekiwaniami dla wszystkich piętnastu zbadanych materiałów. Z uwagi na fakt, że oba zaproponowane w artykule A2 wzory są bezpośrednio połączone z potencjałem międzycząsteczkowym poprzez wykładnik skalujący γ , w omawianej pracy przeprowadziłem dyskusję ich przewidywań dla substancji, których dynamika molekularna zachowuje się w sposób graniczny. Gdy jest ona kontrolowana wyłącznie przez objętość swobodną molekuł ($\gamma \to \infty$), wyprowadzona współzależność pomiędzy

wielkościami termodynamicznymi przyjmuje postać $\Pi_{GT} = \sqrt{\kappa_T \Delta C_p T_g^{-1} \upsilon^{-1} \alpha_p^{-2}}$. W drugim przypadku, tzn. gdy dynamika molekularna kontrolowana jest wyłącznie przez fluktuacje temperatury ($\gamma \to 0$), przejście szkliste występuje w stałej temperaturze. Wobec tego, wartość ciśnieniowego współczynnika temperatury przejścia szklistego powinna wynosić 0, co jest zgodne z przewidywaniami obu zaproponowanych przeze mnie wzorów na dT_g / dp. W tym przypadku wyprowadzona relacja pomiędzy wielościami termodynamicznymi upraszcza się do postaci $\Pi_{GT} = \sqrt{\Delta C_p / \Delta C_\upsilon}$.

3.3. KORELACJA DYNAMICZNEJ HETEROGENICZNŚCI Z INNYMI WIELKOSCIAMI CHARAKTERYZUJACYMI DYNAMIKĘ MOLEKULARNĄ CIECZY PRZECHŁODZONYCH

Zaproponowane przez L. Berthiera i współautorów estymaty stopnia dynamicznej heterogeniczności opierają się na analizie czasów relaksacji strukturalnej. Stało się to motywacją do zbadania korelacji pomiędzy otrzymanymi w powyższy sposób wartościami $\chi_4^{\max}$ a innymi wielkościami bazującymi na analizie relaksacji strukturalnej. Są nimi objętość aktywacji $\upsilon_{act} = RT \left. \frac{\partial \ln \tau}{\partial p} \right|_T$, kruchość izobaryczna $m_p = \left(\partial \log \tau / \partial \left(T_g / T \right) \right)_p \Big|_{T=T_g}$ i izochoryczna $m_\upsilon = \left(\partial \log \tau / \partial \left(T_g / T \right) \right)_\upsilon \Big|_{T=T_g}$. Warto wspomnieć, że współzależność pomiędzy rozmiarem regionów, wewnątrz których ruchy molekuł są od siebie zależne i υ_{act} oraz $m_p - m_\upsilon$, była wcześniej sugerowana przez prof. A. Sokolova[21, 22, 23]. Prace prof. A. Sokolova bazują jednak na rozmiarze

omawianych regionów wyznaczonych za pomocą piku obserwowanego w niskoczęstotliwościowym widmie wibracyjnym, tzw. „boson peak". W kontekście powyższego należy mieć na uwadze, że natura procesu odzwierciedlanego przez „boson peak" jest ciągle dyskutowana w literaturze. Niemniej jednak, istnieje konsensus, iż jest on powiązany z pewną charakterystyczną długością korelacji[24, 25, 26, 27, 28].

Wyniki przeprowadzonych przeze mnie analiz korelacji pomiędzy $\chi_4^{\max}$ a υ_{act} oraz $m_p - m_\upsilon$ zostały przedstawione w artykule A3. Na przykładzie jedenastu przebadanych substancji należących do różnych grup materiałowych wykazałem, że w stałym czasie relaksacji nie występuje żaden ogólny trend wiążący stopień dynamicznej heterogeniczności z objętością aktywacji czy z różnicą pomiędzy izobaryczną i izochoryczną kruchością. Substancje charakteryzujące się zbliżonym stopniem dynamicznej heterogeniczności niekoniecznie posiadają podobne wartości υ_{act} lub $m_p - m_\upsilon$. Szczegółowa analiza pojedynczych substancji w warunkach izochronicznych wykazała, że wraz ze wzrostem ciśnienia stopień dynamicznej heterogeniczności nie zależy liniowo od objętości aktywacji czy różnicy pomiędzy analizowanymi kruchościami, zarówno w skali liniowej, jak i logarytmicznej (istnienie takiej zależności sugerował A. Sokolov). W dalszej części artykułu przeprowadziłem teoretyczne analizy, które precyzują warunki, jakie muszą być spełnione, aby badane korelacje wystąpiły. Mianowicie, aby $\log \chi_4^{\max}$ był liniową funkcją $\log \upsilon_{act}$, wartość wyrażenia $\sqrt{\Delta C_p}\,\frac{dT_g}{dp}$ musi być stała, podczas gdy w przypadku wystąpienia liniowej postaci zależności $\log \chi_4^{\max}\left(\log\left(m_p - m_\upsilon\right)\right)$, wartość wyrażenia $\frac{\left(1+\gamma T\alpha_p\right)^2}{\Delta C_p\left(\gamma T\alpha_p\right)^2}$ powinna być niezmienna. W artykule wykazałem, że oba powyższe wyrażenia w ogólności nie są

stałe w warunkach izochronicznych, co wyklucza istnienie sugerowanych w literaturze liniowych korelacji pomiędzy badanymi wielkościami. Aby zaprezentowana przeze mnie w artykule A3 analiza była kompletna, przedstawione powyżej wyniki potwierdziłem dla różnych warunków izochronicznych.

3.4. UNIWERSALNY WZÓR NA CIŚNIENIOWY WSPÓŁCZYNNIK TEMPERATURY PRZEJŚCIA SZKLISTEGO

Brak liniowych korelacji pomiędzy stopniem dynamicznej heterogeniczności a innymi badanymi w artykule A3 wielkościami charakteryzującymi dynamikę molekularną sugeruje, że wykorzystana w artykule A2 relacja, $\left(\chi_4^H\right)^{\max} \approx \left(\chi_4^T\right)^{\max} + \left(\chi_4^\rho\right)^{\max}$, nie może być w prosty sposób zastąpiona poprzez dowolną zależność wynikającą z analizy czasów relaksacji strukturalnej. Narzuca ona zatem dodatkowy warunek spełniony w przejściu szklistym.

Weryfikacja powyższego wniosku została przedstawiona w artykule A4. Traktując relaksację strukturalną jako funkcję dowolnych dwóch wielkości termodynamicznych, wyprowadziłem uniwersalny wzór, opisujący ciśnieniowy współczynnik temperatury przejścia szklistego, który w zależności od kontrolowanych w eksperymencie warunków termodynamicznych może zostać przekształcony do wielu postaci. Jednakże wszystkie wynikające z niego formy są sobie tożsame. Dowodzi to, że bez nałożenia dodatkowego warunku spełnionego w przejściu szklistym, uzyskanie dwóch niezależnych wzorów na dT_g / dp, a tym samym współzależności alternatywnej do relacji Prigogine'a-Defaya, nie jest możliwe. Warto zaznaczyć, że przedstawiona w artykule analiza, uwzględnia również wykorzystanie wielkości konfiguracyjnych. Traktując relaksację strukturalną jako funkcję temperatury i konfiguracyjnej entropii

oraz konfiguracyjnej objętości, wyprowadziłem wzory, które w granicznym przypadku, gdy $m_T / m_v \to \infty$, (warunek ten opisuje przypadek objętości swobodnej, $m_T = \left(\partial \log \tau / \partial\left(v_g / v\right)\right)_T\Big|_{v=v_g}$ to kruchość izotermiczna) stają się identyczne z wzorami Ehrenfesta. Tak więc dodatkowe obostrzenie ($m_T / m_v \to \infty$) sprawia, że równania Ehrenfesta pomimo, iż mogą zostać wyprowadzone z jednego uniwersalnego wzoru na dT_g / dp, nie są sobie tożsame. Tym samym uzyskana z nich relacja Prigogine'a-Defaya nie jest tautologią. Należy jednak zaznaczyć, że rzeczywiste wartości ilorazu izotermicznej i izochorycznej kruchości znacznie odbiegają od nieskończoności. Zatem otrzymana po uwzględnieniu omawianego warunku relacja nie ma prawa być słuszna dla substancji rzeczywistych. Opierając się na pokazanym w literaturze związku $m_T / m_v = \gamma$ oraz połączeniu pomiędzy wykładnikiem skalującym a wykładnikiem części potencjału międzymolekularnego, która opisuje oddziaływania odpychające, zauważyłem, że relacja Prigogine'a-Defaya powinna być spełniona w przypadku modelowego układu twardych sfer.

Ponadto w artykule A4, przeprowadziłem dyskusję wzorów na ciśnieniowy współczynnik temperatury przejścia szklistego, wyprowadzonych przez prof. J. W. P. Schmelzera[3] z zaproponowanego przez niego ogólnego kryterium dla przejścia szklistego. Na bazie otrzymanego przeze mnie uniwersalnego wzoru na dT_g / dp wykazałem, że przyjęte przez prof. J. W. P. Schmelzera założenie, $\tau_R / T \ll \left(\partial \tau_R / \partial T\right)_p$, w rzeczywistości ogranicza słuszność zaprezentowanych przez niego analiz, wyłącznie do przypadku, w którym objętość jest decydującym czynnikiem determinującym relaksację strukturalną układu, tj. do granicznego przypadku objętości swobodnej. W artykule A4 zauważyłem ponadto, że zastosowania zaprezentowanego przez

J. W. P. Schmelzera ogólnego kryterium dla przejścia szklistego w substancjach podlegających skalowaniu gęstościowemu implikuje wystąpienie przejścia szklistego w stałej objętości (niezależnie od temperatury i ciśnienia), co nie jest prawdą. Sugeruje to zatem niepoprawność zaproponowanego kryterium oraz konieczność jego szczegółowej weryfikacji.

Warto również zaznaczyć, że otrzymane przeze mnie wyniki stały się interesującym komentarzem do jednej z najnowszych prac R. Casaliniego i M. C. Rolanda[29], w której autorzy proponują innowacyjny sposób wyznaczania wykładnika skalującego, bez konieczności wykonywania pomiarów dielektrycznych. Zasugerowali oni połączenie jednego z równań Ehrefesta z równaniem zaprezentowanym przeze mnie w publikacji A1, które wynika bezpośrednio z omawianego uniwersalnego równania opisującego ciśnieniowy współczynnik przejścia szklistego, i które zostało wyprowadzone przez autorów w niezależny sposób. Zabieg ten nie okazał się tautologią, ponieważ jak pokazałem w artykule A4, uzyskanie wzorów Ehrenfesta wymaga przyjęcia dodatkowego warunku, który sprawia, że oba użyte równania stają się niezależne. Należy jednak zwrócić uwagę, iż powyższe założenie powoduje, że zaproponowany przez R. Casaliniego i C. M. Rolanda sposób oszacowywania wykładnika skalującego może okazać się niepoprawny dla pewnych substancji rzeczywistych.

3.5. DALSZE PERSPEKTYWY BADAWCZE

Badania zaprezentowane w artykułach A1-A4 wykazały, że definiowanie przejścia szklistego wyłącznie poprzez ustaloną wartość czasu relaksacji strukturalnej uniemożliwia otrzymanie relacji alternatywnej do relacji Prigogine'a-Defaya. Wyprowadzenie szukanej współzależności jest możliwe wyłącznie po zastosowaniu

dodatkowego, innego niż izochroniczny, warunku spełnionego w przejściu szklistym. Zaproponowana przeze mnie zależność pomiędzy wielkościami termodynamicznymi w przejściu szklistym bazuje na warunku determinowanym poprzez przybliżoną relację pomiędzy estymatami stopnia dynamicznej heterogeniczności (wywołanymi przez fluktuacje entalpi, temperatury i gęstości.) Zatem odnalezienie alternatywnego i eksperymentalnie potwierdzonego warunku, który byłby spełniony podczas przejścia szklistego, wydaje się być jednym z najbardziej ekscytujących kierunków dalszych badań. Genezy powyższego warunku można poszukiwać, zarówno we właściwościach strukturalnych, jak i dynamicznych substancji, jednak te ostatnie wydają się być najbardziej obiecujące. W tym kontekście należy wspomnieć o aktualnie niezwykle interesującym zagadnieniu dynamicznej heterogeniczności i jej wciąż niepoznanym związku z relaksacją strukturalną. Wymaga zauważenia, że eksperymentalne wyznaczenie dynamicznej heterogeniczności poprzez czteropunktową nieliniową funkcję dynamicznej podatności jest trudnym zadaniem. Z uwagi na powyższe, należy wspomnieć o możliwościach jakie dostarczają symulacje komputerowe dynamiki molekularnej, które pozwalają na precyzyjne wyznaczanie wielorzędowych, czasowo-przestrzennych funkcji korelacji (w tym cztero-punktowej funkcji dynamicznej podatności). Zatem, funkcje korelacji, które są niedostępne w standardowych eksperymentach spektroskopowych mogą być badane za pomocą symulacji komputerowych dynamiki molekularnej. Niestety symulacje układów modelujących substancje rzeczywiste znajdujące się w pobliżu przejścia szklistego są niezwykle czasochłonne, dostarczają wielu trudności lub nawet mogą okazać się niemożliwe. Pewnych informacji dotyczących dynamicznej heterogeniczności mogą dostarczyć również atrakcyjne i wciąż rozwijane pomiary trzeciorzędowej nieliniowej funkcji dynamicznej podatności, której amplituda powiązana jest z liczbą dynamicznie

skorelowanych molekuł. Pomiary trzeciorzędowej nieliniowej funkcji dynamicznej podatności zostały już przeprowadzone w pobliżu przejścia szklistego, w warunkach podwyższonego ciśnienia, jednak dla bardzo ograniczonej ilości substancji i na tym etapie, za ich pomocą nie można rzetelnie zweryfikować wyników otrzymanych za pomocą różnorakich estymat jak również symulacji komputerowych dynamiki molekularnej.

Ponadto, nie należy tracić z pola widzenia znaczenia wpływu tempa doprowadzenia układu do punktu transformacji ciecz-szkło na temperaturę przejścia szklistego oraz na czas relaksacji systemu, który charakteryzuje badany proces. Omawiana w poprzednim podrozdziale praca prof. J. W. P. Schmeltzera, jak również ostatnia praca jego autorstwa – Ref. 30, ewidentnie wskazują, że pomimo trwających ponad 60 lat badań, zależność T_g i τ_g od tempa doprowadzenia substancji do przejścia szklistego, w dalszym ciągu pozostaje alternatywą na poznanie dodatkowego kinetyczno-termodynamicznego warunku spełnionego podczas przejścia szklistego.

4. PREZENTACJA OSIĄGNIĘTYCH WYNIKÓW

4.1. CIŚNIENIOWY WSPÓŁCZYNNIK TEMPERATURY PRZEJŚCIA SZKLISTEGO W WARUNKACH SKALOWNAIA GĘSTOŚCIOWEGO

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Referencja: Phys. Rev. E 86, 041502 (2012)

Skrót:

W artykule wskazujemy, że wartości ciśnieniowego współczynnika temperatury przejścia szklistego, dT_g / dp , powszechnie wykorzystywanego do określenia wrażliwości temperatury przejścia szklistego, T_g , na zmianę ciśnienia, mogą być przewidziane w warunkach skalowania gęstościowego. Pokazujemy, że równanie wyprowadzone z warunków izochronicznych przejścia szklistego, połączone ze skalowaniem gęstościowym $Tv^{\gamma} = const.$, z powodzeniem przewiduje wartości dT_g / dp dla różnych substancji formujących szkła, w tym cieczy van der Waalsa, polimerów i cieczy jonowych.

Pressure coefficient of the glass transition temperature in the thermodynamic scaling regime

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(Received 1 June 2012; published 8 October 2012)

We report that the pressure coefficient of the glass transition temperature, dT_g/dp, which is commonly used to determine the pressure sensitivity of the glass transition temperature T_g, can be predicted in the thermodynamic scaling regime. We show that the equation derived from the isochronal condition combined with the well-known scaling, $TV^{\gamma} = \text{const}$, predicts successfully values of dT_g/dp for a variety of glass-forming systems, including van der Waals liquids, polymers, and ionic liquids.

DOI: 10.1103/PhysRevE.86.041502 PACS number(s): 64.70.pm, 62.50.−p, 64.70.Q−

I. INTRODUCTION

The cooling of a liquid, at a constant pressure, is probably one of the most efficient and easiest ways to produce a solid phase. In general, there are two different scenarios. The first one takes place when a liquid turns into a crystalline solid at its freezing temperature. However, it is also possible that some liquids might be cooled below their freezing point without crystallization. On further cooling of the supercooled liquid, a transformation to an amorphous phase might occur. Both liquid-crystal and liquid-glass transitions can be easily identified by, e.g., measuring the temperature dependence of the specific volume $V(T)$. The first transition is manifested by an abrupt and discontinuous change of volume (the first order transition) at the crystallization temperature T_c, whereas the second one shows only a characteristic change in the slope of $V(T)$ at the glass transition temperature T_g. The nature of liquid vitrification has been a subject of great debate during the last decades [1]. Both thermodynamic and kinetic aspects of this transition have been quite extensively discussed in the literature [2]. However, most researchers are now inclined to think about the glass formation as a purely kinetic process and that no thermodynamic phase transition is involved at T_g.

The glass transition temperature alone is an important physical property used to characterize amorphous materials [3]. Beside volumetric measurements, as mentioned already above, there are also other experimental methods useful for determining of T_g. One of the most frequently exploited experimental techniques is differential scanning calorimetry (DSC). Using this technique, the glass transition point is usually defined as an intersection of the DSC curve with a median to the two heat capacity lines representing the glass and liquid behavior. On the other hand, taking into account the kinetic nature of the vitrification process, it is also valid to define T_g as an isochronal or isoviscosity state. According to this view, T_g has been frequently estimated as the temperature at which the structural relaxation time or viscosity is equal, let's say, to 100 s or 10^{12} Pas, respectively. However, it should be pointed out that the isochronal definition is affected by the experiment rate [4] and the isoviscosity one is often not held, e.g., by linear polymers and cross-linked polymers, which do not flow [5].

The glass transition can be induced by varying not only temperature but also pressure [6]. Over the past years much effort has been devoted to investigate the effect of pressure on the glass transition in various types of liquids [7]. From numerous experiments we have learned that the sensitivity of T_g to pressure depends on the nature and type of intermolecular interactions. For instance, a significant shift of T_g is usually observed for van der Waals liquids [8–12], whereas there is only a small pressure effect on the shift of T_g in the case of hydrogen bonded liquids [13,14]. The coefficient dT_g/dp is the most useful and convenient measure of this effect.

Although the glass transition is not a true thermodynamic phase transition, it has some properties of the second order transition. First derivatives of the Gibbs free energy (volume V and entropy S) are continuous, whereas the second ones (heat capacity c_p, thermal expansion coefficient α_p, and compressibility κ_T) change rapidly in the vicinity of T_g, showing a steplike behavior. The values of c_p, α_p, and κ_T are largest in the supercooled state and drop to lower values in the glassy state. For the mentioned above reason, numerous attempts have been made to describe the pressure coefficient of T_g in terms of Ehrenfest equations [15–18]:

$$\left(\frac{dT_g}{dp}\right) = \frac{\Delta\kappa_T}{\Delta\alpha_p}, \tag{1}$$

$$\left(\frac{dT_g}{dp}\right) = \frac{V_g T_g \Delta\alpha_p}{\Delta c_p}, \tag{2}$$

where Δ denotes the difference between the respective coefficients in the liquid and in the glass, and V_g is a specific volume at T_g. It should be stressed that the first equation incorporates the compressibility and the expansion coefficient also measured in the glassy phase, i.e., in the nonequilibrium state. This creates a difficulty in testing the validity of Eq. (1). Indeed, it has been experimentally verified that Eq. (1) is generally not fulfilled [3,19–25], whereas Eq. (2) seems to hold reasonably well for many systems, although not for all. Equation (1) is based on the free volume ideas, while Eq. (2) is based on the entropy approach [26]. Consequently, these results were interpreted as indicating that entropy theories describe the glass transition better than free volume ones [19].

Herein we provide a new equation for the pressure coefficient of the glass transition temperature. We test the proposed relationship using PVT data for several glass-forming liquids representing different groups, i.e, van der Waals liquids, polymers, hydrogen bonding, and ionic liquids.

II. THE PRESSURE COEFFICIENT—ITS FORMULATION, EXPERIMENTAL TEST, AND DISCUSSION

We begin our discussion of dT_g/dp with an analysis of experimental PVT data. Figure 1 shows the V-T dependences measured at various pressures (isobars) for glibenclamide and telmisartan (van der Waals liquids). All the details about PVT measurements can be found in Ref. [27]. PVT data for two other samples, i.e., verapamil hydrochloride (ionic liquid) and polystyrene (PS 168N) with $M_n = 354\,000$ g/mol (polymer) have been already presented in Refs. [27,28]. In order to parameterize the data collected in the supercooled liquid state, we used the following equation of state [29]:

$$v(T,p) = \frac{A_0 + A_1(T - T_0) + A_2(T - T_0)^2}{\{1 + (p - p_0)b_1 \exp[b_2(T - T_0)]\}^{1/\gamma_{EOS}}}, \quad (3)$$

where A_0, A_1, A_2, b_1, b_2, and γ_{EOS} are fitting parameters. The fixed parameters p_0 and T_0 are pressure and temperature in a chosen reference state defined herein by the glass transition temperature at ambient pressure.

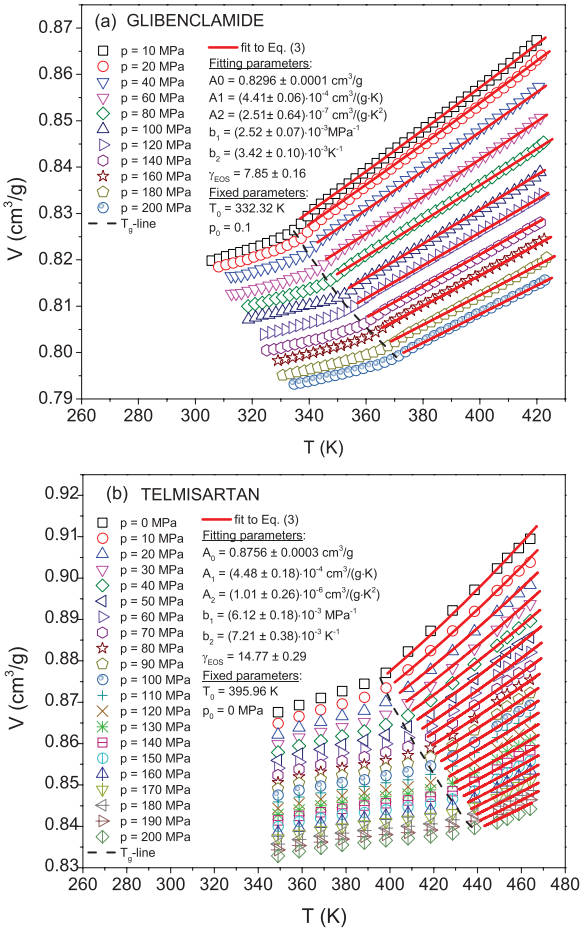

FIG. 1. (Color online) Plots of PVT data for (a) glibenclamide (measured at the cooling rate of 2.5 K/min) and (b) telmisartan (measured at the cooling rate of 1.0 K/min) with their fits to Eq. (3) in the liquid state.

For all analyzed samples, the excellent fits to the experimental data were achieved. The obtained fitting parameters are used next to calculate both the thermal expansion and the compressibility coefficients. The values of the glass transition temperature at various pressures were determined as the temperature of the intersection of two straight lines fitted to a portion of $V(T)$ data above and below the transition region. Determined in this way, values of T_g are plotted as a function of pressure in the insets in the Fig. 2. These experimental dependences were fitted to the phenomenological Andersson-Andersson equation [30]:

$$T_g(p) = T_g^0 \left(1 + \frac{p}{k_1}\right)^{k_2}, \quad (4)$$

where k_1, k_2, and T_g^0 are fitting parameters. From this analysis, we were able to determine the values of the ratio of dT_g/dp in the limit of ambient pressure (see Table I).

As a starting point to find a new equation for the coefficient dT_g/dp, let's focus on the analysis of the experimental dependences of $\log_{10}T_g$ vs $\log_{10}V_g$ for systems studied here. These plots are displayed in Fig. 2. All the $\log_{10}T_g$ data exhibit a linear dependence on $\log_{10}V_g$. From the simple linear regression, one can determine the slope of the dependence, which we denote by the Greek letter γ. The values of the parameter γ are reported in Table I. In addition Fig. 2 also presents T_g determined from the high pressure dielectric measurements. For the considered glass formers, we find that these two different methods of measuring T_g provide consistent results, but not always exactly the same as can be seen in case of polystyrene [Fig. 2(c)]. Taking into account the fact that T_g determined from dielectric measurements was defined at a constant relaxation time, it is now obvious that the dependence $T_g(V_g)$ found for PVT data corresponds well to an isochronal line. However, it should be noted that an isochronal state along a $T_g(V_g)$ line should be in general regarded as an approximation due to the mentioned dependence of T_g on the experiment rate. Taking into account the Deborah number considered by Hodge for the glass transition temperature (Eq. (1) in [4]), one can see that the characteristic time scale for the glass transition, τ_g, can be evaluated more precisely by using the glass transition temperature T_g, the isobaric fragility parameter $m_p = \frac{d\log_{10}\tau}{d(T_g/T)}|_{T_g}$, and the cooling rate q_c in the following way: $\tau_g \approx T_g/(q_c m_p \ln 10)$. Assuming that the glass transition is approached at a constant cooling rate q_c in each isobaric state, the characteristic time scale for this transition depends mainly on the quotient T_g/m_p, which is pressure dependent. A typical behavior of glass forming materials under high pressure is characterized by an increase in T_g and a decrease in m_p with pressure [6]. It implies that T_g/m_p should increase with increasing pressure; however, this quotient established by using experimental data of glass formers is a slowly varying function of pressure, which usually results in the increase in τ_g by only a few seconds with increasing pressure from 0 to 200 to 300 MPa. For instance, the characteristic time scales τ_g of glibenclamide and a prototypical van der Waals liquid phenylphthalein-dimethylether increase by 7 and 9 s, respectively, if pressure increases from 0.1 to 200 MPa and $q_c = 3$ K/min. The pressure effect on the change in τ_g can be neglected especially in the limit of zero pressure in which

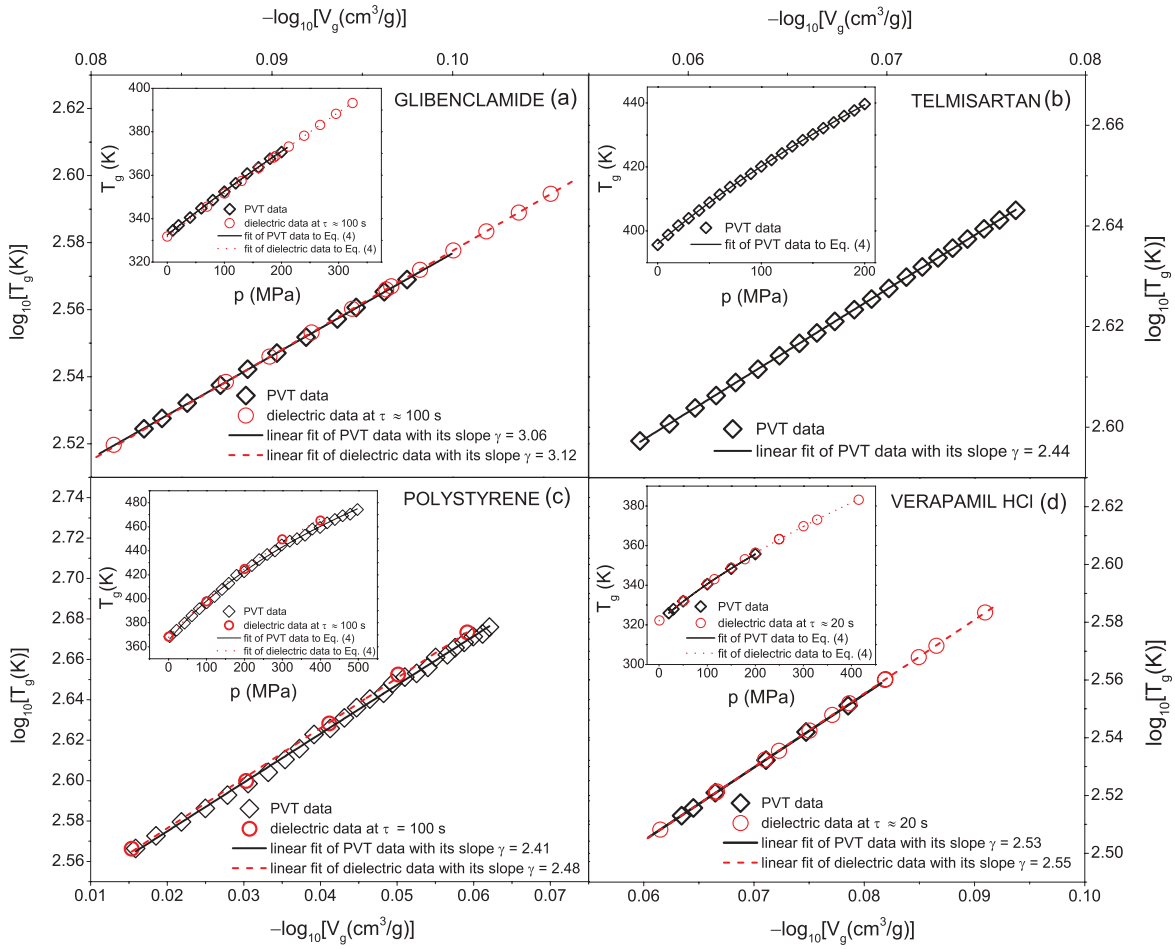

FIG. 2. (Color online) Plots of the dependences of $\log_{10} T_g$ vs $-\log_{10} V_g$ for (a) glibenclamide, (b) telmisartan, (c) polystyrene, and (d) verapamil hydrochloride, which are obtained from PVT and dielectric data (for telmisartan only PVT data are included). The PVT data for verapamile hydrochloride and polystyrene were reported in Refs. [27,28], respectively. All the used dielectric data were reported in Refs. [27,28,53], respectively. The corresponding pressure dependences of the glass transition temperature T_g are shown in the insets.

the pressure coefficient dT_g/dp is usually considered. Since a linear dependence of $\log_{10} T_g$ on $\log_{10} V_g$ has been revealed (Fig. 2), the relationship between T_g and V_g is expected to have the following form:

$$TV^{\gamma} = C \tag{5}$$

TABLE I. Values of the pressure coefficient dT_g/dp in K/MPa in the limit of ambient pressure and the scaling exponent γ, which are based on PVT data analysis.

Material	γ	dT_g/dp from Andersson-Andersson eq. [Eq. (4)]	dT_g/dp from Eq. (9)	dT_g/dp from Ehrenfest eq. [Eq. (1)]	dT_g/dp from Ehrenfest eq. [Eq. (2)]	dT_g/dp from Eq. (10)
Glibenclamide	3.06	0.21	0.21	0.32	0.15[b]	0.60
Telmisartan	2.44	0.28	0.27	0.21	0.30[b]	0.82
Polystyrene	2.41	0.39	0.40	0.51[a]	0.51[a]	1.30
Verapamil HCl	2.53	0.21	0.20	0.18	0.21[b]	0.64

[a]Taken from Ref. [28].
[b]Δc_p required by Eq. (2) has been calculated for glibenclamide, telmisartan, and verapamil HCl by using our unpublished heat capacity data obtained from the differential scanning calorimetry with stochastic temperature modulation.

where C is a constant. It should be noted that Eq. (5) considered for isochronal conditions is a simple consequence of the thermodynamic scaling with the scaling exponent γ [6,31,32].

The next step is to calculate the derivative of the Eq. (5) with respect to temperature that gives

$$\frac{d}{dT}C = V^{\gamma} + T\gamma V^{\gamma-1}\frac{dV}{dT}. \tag{6}$$

Assuming that an isochronal state is a good approximation of the glass transition or simply considering that the differentiation with respect to temperature is performed along the glass transition line in the PVT diagram, the above equation can be rewritten in the following way:

$$0 = V^{\gamma}\left\{1 + \gamma T V^{-1}\left[\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial V}{\partial p}\right)_T \frac{dp}{dT}\right]\right\} \tag{7}$$

and transformed to the form:

$$0 = 1 + \gamma T V^{-1}\left(\frac{\partial V}{\partial T}\right)_p + \gamma T V^{-1}\left(\frac{\partial V}{\partial p}\right)_T \frac{dp}{dT}. \tag{8}$$

Finally, we arrive at the new relation describing the coefficient dT_g/dp:

$$\frac{dT_g}{dp} = \frac{\gamma T_g \kappa_T}{1 + \gamma T_g \alpha_p}. \tag{9}$$

It should be emphasized that the right side of the Eq. (9) includes thermodynamic coefficients in the equilibrium supercooled liquid state. Thus, there is no need to measure values in the nonequilibrium glassy phase as, for example, in the case of the Eq. (1).

In order to check a validity of the newly derived relationship we have calculated values of both thermal expansion and compressibility coefficients of supercooled liquid at T_g using fitting parameters previously found from the analysis of PVT data using the equation of state [Eq. (3)]. Having determined values of all the parameters in Eq. (9), we can calculate the value of the coefficient dT_g/dp. Comparison of the values of dT_g/dp determined from Eq. (9) and from the analysis of the $T_g(p)$ line shows a good agreement for systems studied here (Table I). On the other hand, the first Ehrenfest equation (1) does not give us correct values of dT_g/dp (Table I).

Next, we should answer the following question: What is the physical meaning of the exponent γ in Eq. (9). In the last decade, a new approach to the analysis and description of structural relaxation times and viscosity of glass-forming liquids, called thermodynamic scaling, was introduced [33–36]. According to this concept, the different isobaric and isothermal dependences of structural relaxation times/viscosity can be collapsed onto a single scaling curve if they are plotted as a function of TV^{γ}. Since it has been already pointed out that $T_g(V_g)$ is an isochronal line, the exponent γ in Eq. (9) can be identified with one appearing in the thermodynamic scaling law. This is confirmed when the dielectric relaxation times of each system examined here are plotted versus $T^{-1}V^{-\gamma}$ using the γ exponent value determined from its PVT data (see Fig. 3 and Table I). In order to answer the question we posed earlier, it should be noted that the scaling exponent γ has been related to the effective exponent m used to model the repulsive part of the intermolecular potential in dense systems, r^{-m}, $m = 3\gamma$. In a limiting case when the exponent tends to infinity, the hard sphere type of interaction becomes dominating. Then, the free volume is the key factor controlling the molecular dynamics. For this limiting case our new equation for the pressure coefficient of the glass transition temperature takes the following simple form:

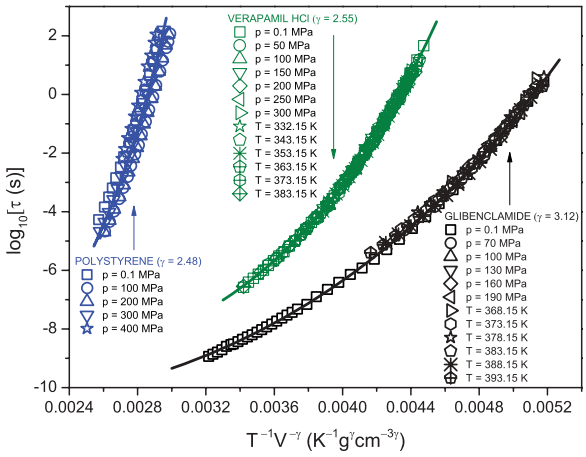

FIG. 3. (Color online) The TV^{γ}-scaling plot of structural relaxation times τ for glibenclamide, verapamil hydrochloride, and polystyrene. The used dielectric data were earlier reported in Refs. [27,28,53], respectively.

$$\frac{dT_g}{dp} = \frac{\kappa_T}{\alpha_p}. \tag{10}$$

In this context, it should be mentioned that very recently, the same equation has been derived by Schmelzer [18]. Similarly to us, Schmelzer claims that Eq. (10) is valid only if molecular dynamics of glass-forming liquids can be described by the free volume concepts.

To demonstrate the general applicability of Eq. (9), we performed another test. Using the earlier reported dielectric and PVT data for commonly known glass formers, such as orthoterphenyl (OTP) [37,38], phenylphthalein-dimethylether (PDE) [39,40], 1,1′-bis (p-methoxyphenyl) cyclohexane (BMPC) [10,41], propylene carbonate (PC) [42,43], salol [12,44], and glycerol [43,45], we compared the values of dT_g/dp established from the dielectric data at ambient pressure to those determined from Eq. (9) with the scaling exponent γ also found from dielectric data. Table II presents a good agreement between the values of dT_g/dp predicted from the Eq. (9) and those found from the phenomenological relationships [e.g., Eq. (4)].

As mentioned the right hand side of the Schmelzer equation [Eq. (10)] can be also derived as the limiting case when our formula for dT_g/dp given by Eq. (9) tends to infinity. Then, the right hand side of Eq. (9) approaches its upper limit in terms of the possible values of the exponent γ. This implication of Eq. (9) explains why Eq. (10) yields the values of dT_g/dp (see Tables I and II), which are considerably larger than those predicted by using our equation for dT_g/dp [Eq. (9)] that are in a very good agreement with those determined directly from the experimental dependences $T_g(p)$. The overestimated

TABLE II. Values of the pressure coefficient dT_g/dp in K/MPa in the limit of ambient pressure and the scaling exponent γ, which are based on dielectric data analysis. Only the isobaric expansivity and the isothermal compressibility are calculated in Eqs. (9) and (10) from PVT data.

Material	γ	dT_g/dp from Andersson-Andersson eq. [Eq. (4)]	dT_g/dp from Eq. (9)	dT_g/dp from Eq. (10)
OTP	4.40[a]	0.26	0.26	0.61
PDE	4.38[a]	0.26	0.26	0.60
BMPC	7.84[a]	0.24	0.22	0.36
PC	4.20[b]	0.09	0.10	0.31
Salol	5.20[c]	0.20	0.19	0.42
Glycerol	1.40[b]	0.05	0.04	0.36

[a]From Ref. [52].
[b]From Refs. [43,45].
[c]From Ref. [7].

character of Eq. (10) found for the tested materials is a natural consequence of the fact that molecular dynamics of real glass formers is governed by both the thermal activations and the free volume changes, and the pure free volume is only one of the extreme ideal cases [6,7,34,46–51].

III. SUMMARY

In this paper, a new equation for the pressure coefficient of the glass transition temperature, dT_g/dp, is obtained and successfully tested for several glass-forming liquids. The derivative dT_g/dp is defined by thermodynamic coefficients characterizing solely the supercooled liquid state. Moreover, in the case when the free volume becomes a key factor governing molecular dynamics, our equation is transformed to the simpler form being consistent with the equation recently derived by Schmelzer.

ACKNOWLEDGMENTS

K.K., A.G., K.G., Z.W., and M.P. gratefully acknowledge financial support from the Polish National Science Centre within the program MAESTRO 2. K.K is deeply thankful for the stipend received within the project "DoktoRIS - The Stipend Program for the Innovative Silesia," which is cofinanced by the EU European Social Fund. A.P.S. acknowledges partial financial support from the NSF Polymer program (DMR-1104824).

[1] J. W. P. Schmelzer and I. Gutzow, *Glasses and the Glass Transition* (Wiley VCH, Berlin, 2011).
[2] P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University Press, Princeton, NJ, 1996).
[3] M. Goldstein, J. Phys. Chem. **77**, 667 (1973).
[4] I. M. Hodge, J. Non-Cryst. Solids **169**, 211 (1994).
[5] D. J. Plazek and K. L. Ngai, in *Physical Properties of Polymers Handbook*, 2nd ed., edited by J. E. Mark (Springer-Verlag, Berlin, 2007), Chap. 12.
[6] G. Floudas, M. Paluch, A. Grzybowski, and K. Ngai, in *Molecular Dynamics of Glass-Forming Systems: Effects of Pressure*, edited by Friedrich Kremer, Advances in Dielectrics (Springer-Verlag, Berlin, 2011).
[7] C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).
[8] M. Paluch, S. Hensel-Bielowka, and T. Psurek, J. Chem. Phys. **113**, 4374 (2000).
[9] M. Paluch, J. Chem. Phys. **115**, 10029 (2001).
[10] S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, J. Chem. Phys. **117**, 2317 (2002).
[11] R. Casalini, M. Paluch, J. J. Fontanella, and C. M. Roland, J. Chem. Phys. **117**, 4901 (2002).
[12] R. Casalini, M. Paluch, and C. M. Roland, J. Phys. Chem. A **107**, 2369 (2003).
[13] S. Pawlus, M. Paluch, J. Ziolo, and C. M. Roland, J. Phys.: Condens. Matter **21**, 332101 (2009).
[14] M. Paluch, S. Pawlus, A. Grzybowski, K. Grzybowska, P. Wlodarczyk, and J. Ziolo, Phys. Rev. E **84**, 052501 (2011).
[15] N. Hirai and H. Eyring, J. Polym. Sci. **37**, 51 (1959).
[16] I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans-Green, New York, 1954), Chap. 19.
[17] Th. M. Nieuwenhuizen, Phys. Rev. Lett. **79**, 1317 (1997).
[18] J. W. P. Schmelzer, J. Chem. Phys. **136**, 074512 (2012).
[19] M. Goldstein, J. Chem. Phys. **39**, 3369 (1963).
[20] R. O. Davies and G. O. Jones, Adv. Phys. **2**, 370 (1953).
[21] J. M. O'Reilly, J. Polym. Sci. **57**, 429 (1962).
[22] U. Bianchi, J. Phys. Chem. **69**, 1497 (1965).
[23] E. N. Dalal and P. J. Phillips, Macromolecules **16**, 890 (1983).
[24] M. Naoki, K. Matsumoto, and M. Matsushita, J. Phys. Chem. **90**, 4423 (1986).
[25] S. Ichihara, A. Komatsu, Y. Tsujita, T. Nose, and T. Hata, Polym. J. **2**, 530 (1971).
[26] S. Takahara, O. Yamamuro, and H. Suga, J. Non-Cryst. Solids **171**, 259 (1994).
[27] Z. Wojnarowska, M. Paluch, A. Grzybowski, K. Adrjanowicz, K. Grzybowska, K. Kaminski, P. Wlodarczyk, and J. Pionteck, J. Chem. Phys. **131**, 104505 (2009).
[28] S. Barry, Ph.D. thesis, The Ulm University, Germany, 1992.
[29] A. Grzybowski, K. Grzybowska, M. Paluch, A. Swiety, and K. Koperwas, Phys. Rev. E **83**, 041505 (2011).
[30] S. Andersson and O. Andersson, Macromolecules **31**, 2999 (1998).
[31] M. Paluch, K. Grzybowska, and A. Grzybowski, J. Phys.: Condens. Matter **19**, 205117 (2007).
[32] U. R. Pedersen, N. Gnan, N. P. Bailey, T. B. Schrøder, and J. C. Dyre, J. Non-Cryst. Solids **357**, 320 (2011).
[33] C. Dreyfus, A. Aouadi, J. Gapinski, M. Matos-Lopes, W. Steffen, A. Patkowski, and R. M. Pick, Phys. Rev. E **68**, 011204 (2003).
[34] R. Casalini and C. M. Roland, Phys. Rev. E **69**, 062501 (2004).
[35] C. Dreyfus, A. Le Grand A, J. Gapinski, W. Steffen, and A. Patkowski, Eur. Phys. J. B **42**, 309 (2004).
[36] C. Alba-Simionseco, A. Cailliaux, A. Alegria, and G. Tarjus, Europhys. Lett. **68**, 58 (2004).

[37] M. Naoki, H. Endou, and K. Matsumoto, J. Phys. Chem. **91**, 4169 (1987).
[38] M. Naoki and S. Koeda, J. Phys. Chem. **93**, 948 (1989).
[39] M. Paluch, R. Casalini, and C. M. Roland, Phys. Rev. B **66**, 092202 (2002).
[40] M. Paluch, R. Casalini, A. Best, and A. Patkowski, J. Chem. Phys. **117**, 7624 (2002).
[41] M. Paluch, C. M. Roland, R. Casalini, G. Meier, and A. Patkowski, J. Chem. Phys. **118**, 4578 (2003).
[42] S. Pawlus, R. Casalini, C. M. Roland, M. Paluch, S. J. Rzoska, and J. Ziolo, Phys. Rev. E **70**, 061501 (2004).
[43] A. Reiser, G. Kasper, and S. Hunklinger, Phys. Rev. B **72**, 094204 (2005); **74**, 019902(E) (2006).
[44] L. Comez, S. Corezzi, D. Fioretto, H. Kriegs, A. Best, and W. Steffen, Phys. Rev. E **70**, 011504 (2004).
[45] K. Z. Win and N. Menon, Phys. Rev. E **73**, 040501(R) (2006).
[46] M. L. Ferrer, C. Lawrence, B. G. Demirjin, D. Kivelson, C. Alba-Simonesco, and G. Tarjus, J. Chem. Phys. **109**, 8010 (1998).
[47] M. Paluch, R. Casalini, and C. M. Roland, Phys. Rev. B **66**, 092202 (2002).
[48] R. Casalini and C. M. Roland, J. Chem. Phys. **119**, 4052 (2003).
[49] C. M. Roland, M. Paluch, T. Pakula, and R. Casalini, Philos. Mag. B **84**, 1573 (2004).
[50] G. Tarjus, D. Kivelson, S. Mossa, and C. Alba-Simionesco, J. Chem. Phys. **120**, 6135 (2004).
[51] K. Adrjanowicz, A. Grzybowski, K. Kaminski, and M. Paluch, Mol. Pharmaceutics **8**, 1975 (2011).
[52] A. Grzybowski, M. Paluch, K. Grzybowska, and S. Haracz, J. Chem. Phys. **133**, 161101 (2010).
[53] Z. Wojnarowska, K. Adrjanowicz, K. Kaminski, L. Hawelek, and M. Paluch, J. Phys. Chem. B **114**, 14815 (2010).

4.2. WPŁYW DYNAMICZNEJ HETEROGENICZNOŚCI I SKALOWANIA GĘSTOŚCIOWEGO DYNAMIKI MOLEKULARNEJ NA RELACJĘ POMIĘDZY WSPÓŁCZYNNIKAMI TERMODYNAMICZNYMI W PRZEJŚCIU SZKLISTYM

Autorzy:

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Referencja: J. Chem. Phys. 143, 024502 (2015)

Skrót:

W artykule, biorąc pod uwagę kinetyczne pochodzenie przejścia szklistego, definiujemy i eksperymentalnie weryfikujemy termodynamiczne cechy tego procesu. Wykorzystując skalowanie gęstościowe i czteropunktową miarę dynamicznej heterogeniczności dynamiki molekularnej cieczy formujących szkła, badamy wkłady fluktuacji entalpi, temperatury i gęstości do przestrzennie heterogenicznej dynamiki molekularnej, znajdując wzór na ciśnieniowy współczynnik temperatury przejścia szklistego, dT_g / dp. Uzyskane równanie, w połączeniu z poprzednio wyprowadzonym przez nas, wyłącznie w warunkach skalowania gęstościowego, równaniem na dT_g / dp, implikuje relację pomiędzy współczynnikami termodynamicznymi w T_g. Ponieważ uzyskana relacja i oba równania na dT_g / dp są potwierdzone przez analizę danych eksperymentalnych w T_g, stają się one interesującą alternatywą dla klasycznej relacji Prigogine'a-Defaya i wzorów Ehrenfesta w przypadku przejścia ciecz-szkło.

Effects of dynamic heterogeneity and density scaling of molecular dynamics on the relationship among thermodynamic coefficients at the glass transition

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(Received 12 March 2015; accepted 15 June 2015; published online 8 July 2015)

In this paper, we define and experimentally verify thermodynamic characteristics of the liquid-glass transition, taking into account a kinetic origin of the process. Using the density scaling law and the four-point measure of the dynamic heterogeneity of molecular dynamics of glass forming liquids, we investigate contributions of enthalpy, temperature, and density fluctuations to spatially heterogeneous molecular dynamics at the liquid-glass transition, finding an equation for the pressure coefficient of the glass transition temperature, dTg/dp. This equation combined with our previous formula for dTg/dp, derived solely from the density scaling criterion, implies a relationship among thermodynamic coefficients at Tg. Since this relationship and both the equations for dTg/dp are very well validated using experimental data at Tg, they are promising alternatives to the classical Prigogine-Defay ratio and both the Ehrenfest equations in case of the liquid-glass transition. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4923005]

I. INTRODUCTION

Over the past decades, the experimental results of the high pressure studies of supercooled liquids have distinctly advanced our understanding of the liquid-glass transition phenomenon. A lot of studies have been focused on investigating the effect of the pressure on the glass transition temperature T_g. A natural measure of this effect for given material is the pressure coefficient of the glass transition temperature dT_g/dp. From numerous experimental studies of different glass-formers, it was found that in case of van der Waals liquids,[1–5] the change of the pressure usually brings about a significant change of T_g (for those materials, typical increase in T_g caused by increase in pressure of 1 MPa amounts about 0.25 K), whereas values of dT_g/dp are rather small for hydrogen bonded liquids[6,7] (usually they are not greater than 0.1 K/MPa). However, a central issue is to establish a relationship between dT_g/dp and key thermodynamic coefficients, i.e., isobaric expansivity α_p, isothermal compressibility κ_T, and isobaric C_p and isochoric C_υ specific heats.

At the glass transition region, first derivatives of the Gibbs free energy (volume υ and entropy S) are continuous, whereas second ones, which are reflected in the thermodynamic coefficients, show step-like behavior in the vicinity of T_g, and for that reason, the liquid-glass transition was tried to consider as the second order phase transition. Consequently, some efforts were undertaken to verify both the Ehrenfest equations (Eqs. (1a) and (1b))[8–10] and the Prigogine-Defay ratio (Eq. (2)),

$$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_p}, \tag{1a}$$

$$\frac{dT_g}{dp} = \upsilon T_g \frac{\Delta\alpha_p}{\Delta C_p}, \tag{1b}$$

and

$$\Pi = \frac{1}{\upsilon T_g}\frac{\Delta C_p \Delta\kappa_T}{(\Delta\alpha_p)^2} \equiv 1, \tag{2}$$

where Δ denotes the differences between respective coefficients in the liquid and in the glassy states, i.e., in the two phases which coexist at transition point. Equation (2) is a combination of Eqs. (1a) and (1b). However, the vast majority of experimental tests revealed that the value of the Prigogine-Defay ratio is usually significantly larger than unity,[8,11–14] because Eq. (1a) is usually not satisfied.[15–22] In this context, it should be noted that Eq. (1a) incorporates κ_T, which is also measured in the glassy state, i.e., in the nonequilibrium state, which makes serious difficulties in its experimental verification.[23] On the other hand, Eq. (1b) seems to hold reasonably well for many systems, although not for all. Nevertheless, the Ehrenfest equations are generally recognized as not being fulfilled at the glass transition, due to this process being suspected of having rather kinetic than thermodynamic origin.

In this paper, according to general wisdom, we consider the glass transition as a kinetic process and consequently on this basis we derive the new equation for dT_g/dp. This new equation takes into account how fluctuations of enthalpy, temperature, and density affect the dynamics of supercooled liquids. Moreover, we use it to establish the relationship among thermodynamic coefficients at glass transition. It is worth

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noting that correct relation among thermodynamic coefficients at the glass transition has been prospected since analysis of the Prigogine-Defay ratio revealed that it is not fulfilled for the glass transition, i.e., since 1950s. Thus, it should be emphasized that our new relationship among thermodynamic coefficients at the glass transition turns out to be correct for all 15 examined glass-formers.

II. DETERMINATION OF THE EXPERIMENTAL VALUE OF THE PRESSURE COEFFICIENT OF THE GLASS TRANSITION TEMPERATURE

Before starting a derivation of the new equation for dT_g/dp, we will briefly discuss strategy applied for determining experimental values of this coefficient. As a first step, one should experimentally determine a dependence of T_g on the pressure. Since the glass transition is manifested by a characteristic change in the dependence $\upsilon(T)$ (see Fig. 1, where volumetric measurement for Carvedilol Base CB is presented), the value of T_g at given pressure can be determined by intersection of two lines, which describes the dependence $\upsilon(T)$ below and above T_g near the glass transition.

Another experimental method, which allows determination of T_g, is differential scanning calorimetry (DSC). Using this technique, the glass transition point is usually defined as an intersection of the DSC curve with a median to the two heat capacity lines representing the glass and the liquid behavior. Unfortunately, this method is not easy to apply at elevated pressure. On the other hand, an excellent experimental tool to detect changes of T_g with compression is high pressure dielectric spectroscopy. Considering the glass transition as a kinetic process, the glass transition can be defined as a state, at which the structural relaxation time τ achieves some characteristic value.[25] Our analysis of volumetric and dielectric measurements reveals that the glass transition for CB takes place at a constant structural relaxation time, i.e., $\log(\tau/s) = 1.625$. The dependence $T_g(p_g)$ obtained from high pressure dielectric measurements is in perfect agreement with one determined from volumetric measurements. Moreover, at ambient pressure, the values of T_g are equal to the value of T_g determined from the analysis of dependence $C_p(T)$ measured by DSC with stochastic temperature modulation, see the inset in Fig. 1 (and the supplementary material[26] where details of our analysis are presented). The experimental dependence $T_g(p_g)$ enabled us to determine the reference value of dT_g/dp for each material at ambient pressure.

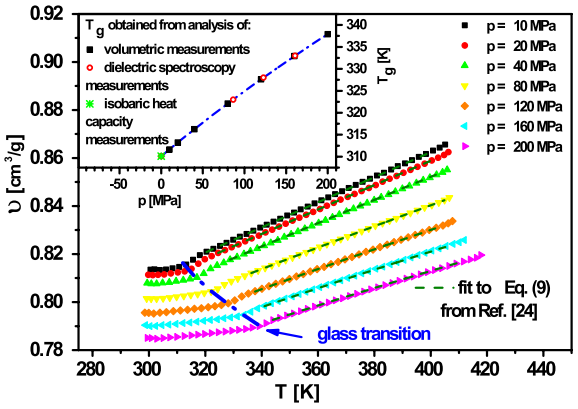

FIG. 1. Plot of volumetric data for carvedilol base with their fits to Eq. (9) from Ref. 24 in the liquid state. In the inset, the dependence $T_g(p_g)$ obtained for carvedilol base from analysis of volumetric and dielectric measurements. The glass transition for carvedilol base takes place at constant structural relaxation time, for which $\log(\tau/s) = 1.625$. Moreover, at ambient pressure, value of T_g determined from analysis of isobaric heat capacity measurement is plotted. Cooling rates applied in all experiments equal 0.5 K/min. The dotted-dashed line denotes the curve of the numerical interpolation of experimental data.

III. THE NEW EQUATION FOR THE PRESSURE COEFFICIENT OF THE GLASS TRANSITION TEMPERATURE

In order to derive the new equation for dT_g/dp, we took into account a fundamental aspect of molecular dynamics of glass-forming liquids, i.e., its heterogeneous nature. During the cooling or compression, the distances between molecules become shorter and their movements become dependent on each other. It implies that inside a supercooled liquid, the regions, within which rearrangements of molecules are cooperative, are formed, as suggested already by Adam and Gibbs in 1965.[27] Later works have shown that the sizes of those regions do not have to be constant in time and/or space[28,29] and that the dynamics of molecules, which belong to different regions, are not identical.[30–33] Thus, the dynamics of whole system is heterogeneous. Recently, to accurately quantify the dynamic heterogeneity, the four-point time-dependent function, called dynamic susceptibility $\chi_4(t)$, has been suggested. The amplitude of the peak of this function $\chi_4^{\max}$ is accepted as a good measure of the number of dynamically correlated molecules[34] or the size of the regions, within which the molecular dynamics is correlated.[35] Unfortunately, the experimental measurement of dynamic susceptibility is not accessible in standard spectroscopy method because it requires detecting fourth order nonlinear susceptibility, which is still a challenging task. It is worth noting that the promising experimental idea is a measurement of the third order nonlinear dielectric susceptibility $\chi_3(t)$, which provides us, however, only an evaluation of the number of dynamically correlated molecules[36,37] and cannot give us the complete information about the dynamic heterogeneity in the spatial and temporal domains in contrast to the four-point correlation function $\chi_4(t)$. Since a direct measurement of $\chi_4(t)$ is not possible, the indirect analysis of dynamic susceptibility, which gives information about the response of dynamic susceptibility to a perturbing field, has been found useful. It is worth mentioning that the above analysis uses the estimates of the four-point time dependent function, which are based on the two-point time-dependent correlator that is accessible in the standard spectroscopy methods. A brief consideration of the theoretical basis for this study is presented in the supplementary material.[26] It should be noted that indirect analysis of $\chi_4(t)$ is still fervently discussed,[38–40] nevertheless $\chi_4^{\max}$ remains a good estimate of the measure of the dynamic heterogeneity.[34,35,41–45] Using the above investigation, Berthier *et al.*[34,35] derived the expressions for the estimates of measures

of the contributions to the dynamic heterogeneity induced by the fluctuations of enthalpy, temperature, and density, given, respectively, by $(\chi_4^H)^{\max} \approx \frac{k_B T^2}{\Delta C_p}\left(\frac{\beta}{e}\frac{\partial \ln \tau}{\partial T}\big|_p\right)^2$, $(\chi_4^T)^{\max} \approx \frac{k_B T^2}{\Delta C_v}\left(\frac{\beta}{e}\frac{\partial \ln \tau}{\partial T}\big|_v\right)^2$, and $(\chi_4^\rho)^{\max} \approx k_B T \kappa_T \rho^3 \left(\frac{\beta}{e}\frac{\partial \ln \tau}{\partial \rho}\big|_T\right)^2$, where k_B is a Boltzmann constant and β is a stretching parameter of a two-point correlation function (e.g., Kohlrausch-Williams-Watts function $\Phi(t) = \exp\left[-(t/\tau_\alpha)^\beta\right]$). The authors also established a direct relationship among them $(\chi_4)^{\max} \approx (\chi_4^H)^{\max} \approx (\chi_4^T)^{\max} + (\chi_4^\rho)^{\max}$. The high pressure experimental examination of the aforementioned relationship as well as its simple verification in terms of the relative role of temperature and density fluctuations in the molecular dynamics of the examined glass formers near the glass transition confirmed[46] that the configurational values of the heat capacities should be used in the estimates $(\chi_4^H)^{\max}$ and $(\chi_4^T)^{\max}$ (as previously suggested in Ref. 35) to minimalize the contributions to the fluctuations unrelated to the glassy dynamics in real molecular systems.

Since the structural relaxation time is constant at the glass transition, a complete derivative of dependence $\tau(T,p)$ equals 0 and therefore can be transformed to $\frac{dT}{dp} = -\left(\frac{\partial \log \tau}{\partial p}\right)_T / \left(\frac{\partial \log \tau}{\partial T}\right)_p$. Employing the approximation of the degrees of the dynamic heterogeneity induced by fluctuations of density $(\chi_4^\rho)^{\max}$ and enthalpy $(\chi_4^H)^{\max}$, one obtains a succeeding equation $\left(\frac{dT}{dp}\right)^2 = \frac{T v \kappa_T}{\Delta C_p}\frac{(\chi_4^\rho)^{\max}}{(\chi_4^H)^{\max}}$, which can be rewritten as follows: $\left(\frac{dT}{dp}\right)^2 \approx \frac{T v \kappa_T}{\Delta C_p}\left(\frac{(\chi_4^H)^{\max} - (\chi_4^T)^{\max}}{(\chi_4^H)^{\max}}\right)$. The useful form of the quotient $\frac{(\chi_4^H)^{\max}}{(\chi_4^T)^{\max}} \approx 1 + \kappa_T T \Delta C_v \gamma^2 \rho$ can be derived after employing the power law density scaling idea as follows from Eq. (21) in Ref. 34. According to the power law density scaling of molecular dynamics, the temperature-volume dependence of structural relaxation times $\tau(T,v)$ can be described in terms of a single scaling variable Tv^γ. Since a linear dependence of $\log(T)|_\tau$ on $\log(v)|_\tau$ has been revealed by the analysis of experimental data, the relation between $T|_\tau$ and $v|_\tau$ is expected to have the following form: $Tv^\gamma = C$, and the scaling exponent γ can be easily determined from the linear dependence $\log T_\tau(\log v_\tau)$ (see the supplementary material,[26] where the detailed analysis of density scaling for CB is presented). It is worth noting that the density scaling has been experimentally validated for more than 100 van der Waals liquids and polymers. In the case of hydrogen bonded liquids, a deviation of experimental data from scaling function is observed. However, our study does not demand a superposition of the values of Tv^γ for each structural relaxation time, but only at the structural relaxation time corresponding to the glass transition, it means that just the linear dependence of $\log T_g$ on $\log v_g$ must be observed. It is worth mentioning that a dependence of scaling exponent on the structural relaxation time has been previously suggested[47,48] for some materials. In this case, the thermodynamic scaling with a constant value of γ is not observed. Nevertheless, it does not exclude the aforementioned linear dependence at the glass transition and we can use the expression for $(\chi_4^H)^{\max}/(\chi_4^T)^{\max}$ derived in terms of density scaling also for those materials, e.g., hydrogen bonded liquids. In this way, we obtain the sought after new expression for the pressure coefficient of the glass transition temperature,

$$\frac{dT_g}{dp} \approx T_g \kappa_T \gamma \left(\frac{\Delta C_p}{\Delta C_v} + \gamma^2 \kappa_T T_g \rho \Delta C_p\right)^{-1/2}. \tag{3}$$

Our new equation for dT_g/dp can be used to establish the new relation among thermodynamic coefficients at the glass transition. For this purpose, we use our recently proposed another equation for the pressure coefficient of the glass transition temperature,

$$\frac{dT_g}{dp} = \frac{\gamma T_g \kappa_T}{1 + \gamma T_g \alpha_p}, \tag{4}$$

which was derived from the isochronal definition of the glass transition and from the observed linear dependence of $\log T_g$ on $\log v_g$. It should be stressed that the predictions dT_g/dp based on Eq. (4) were experimentally verified for various glass forming liquids.[49] Herein, dividing Eq. (4) by Eq. (3), we obtain the new equation,

$$\Pi_{GT} = \frac{\left(\frac{\Delta C_p}{\Delta C_v} + \gamma^2 \kappa_T T_g \rho \Delta C_p\right)^{1/2}}{1 + \gamma T_g \alpha_p} \approx 1, \tag{5}$$

which describes the relationship among thermodynamic coefficients at the glass transition (GT); thus, it is substitute of the Prigogine-Defay ratio for this process. Since the glass transition has a kinetic, not thermodynamic, origin according to the general wisdom, Eq. (5) should better describe the relationship among thermodynamic coefficients at this transition than the Prigogine-Defay ratio.

IV. RESULTS AND DISCUSSION

Now, we present the results of the experimental verification of our new equations, whereas the detailed description of our analysis is shown in the supplementary material.[26] It should be noted that calculations of ΔC_v require measurements of dependences $v(T,p)$ for glass, which were not performed for some of the examined glass formers. However, we observed that for the analyzed materials, for which the dependences $v(T,p)$ in the glassy state were measured, values of $\Delta C_p/\Delta C_v$ differ slightly from each other. Therefore, in case of other materials, we use the average value of $\Delta C_p/\Delta C_v = 1.66$ to determine the predictions based on our new equations (Eqs. (3) and (5)). The results of our analysis as well as the experimental values of the pressure coefficient of T_g are presented in Table I. Equations (3) and (4) correctly predict the experimental values of dT_g/dp for all examined materials.

Since the correctness of both our equations for dT_g/dp has been experimentally confirmed, Π_{GT} is expected to be equal to 1. Indeed, differences between experimental values of Π_{GT} and unity are not larger than 16% for all of the 15 studied glass formers. It should be stressed that for the materials, for which the values of $\Delta C_p/\Delta C_v$ were calculated from experimental data, avoiding their approximation, the differences between the experimental value of Π_{GT} and 1 are smaller than 9%. Thus, we can accept that Π_{GT} properly describes the relationship among thermodynamic coefficients at the glass transition. In the context of our results, it is worth noting that the predictions

TABLE I. Values of dT_g/dp in K/MPa calculated at ambient pressure (except of mixture of 67% *o*-terphenyl and 33% *o*-phenylphenol OTP-OPP, for which $p = 28.8$ MPa). The reference values, which are obtained by analysis of the experimental measurements, and the results consistent with them, are bold. In the last two columns, the predictions of Π_{GT} and Π are presented. In those columns, the boldface values do not differ from the theoretical expectations by more than 15%. The results, which are obtained by using the approximate value $\Delta C_p/\Delta C_v \approx 1.66$, are denoted by the symbol $*$.

	dT_g/dp obtained from:					Π_{GT}	Π
Material	Analysis of experimental measurements	Equation (3)	Equation (4)	Equation (1a)	Equation (1b)	Equation (5)	Equation (2)
Carvedilol base	**0.16 ± 0.01**	**0.16 ± 0.02**	**0.16 ± 0.01**	0.21 ± 0.02	0.13 ± 0.02	**0.97 ± 0.13**	1.61 ± 0.12
Ortho-terphenyl	**0.26**[a]	**0.28 ± 0.05**	**0.26 ± 0.01**[b]	0.39 ± 0.02	0.17 ± 0.05	**0.93 ± 0.19**	2.25 ± 0.16
Glibenclamide	**0.21 ± 0.01**[b]	**0.23 ± 0.01**	**0.21 ± 0.01**[b]	0.32 ± 0.03	0.14 ± 0.04	**0.92 ± 0.20**	2.30 ± 0.17
Polystyrene	**0.39 ± 0.01**[b]	**0.41 ± 0.13**	**0.40 ± 0.02**[b]	0.50 ± 0.03	0.29 ± 0.04	**0.96 ± 0.28**	1.73 ± 0.13
Telmisartan	**0.28 ± 0.01**[b]	**0.27 ± 0.10**	**0.27 ± 0.01**[b]	0.21 ± 0.02	**0.30 ± 0.03**	**1.03 ± 0.38**	0.74 ± 0.13
Verapamil hydrochlorine	**0.21 ± 0.01**[b,c]	**0.19 ± 0.03**	**0.20 ± 0.01**[b]	**0.19 ± 0.02**	0.25 ± 0.03	**1.05 ± 0.13**	0.77 ± 0.14
OTP-OPP		0.24 ± 0.02	0.24 ± 0.01	0.27 ± 0.02[d]	0.22 ± 0.03[d]	**0.98 ± 0.14**	1.20 ± 0.13[d]
Glycerol	**0.05 ± 0.01**[b]	**0.05 ± 0.01***	**0.06 ± 0.01**			1.16 ± 0.02*	3.7[e]
Triethyl-2-acetylcitrate	**0.13 ± 0.01**	**0.13 ± 0.01***	**0.13 ± 0.01**			**0.97 ± 0.02***	
Salol	**0.20 ± 0.01**[b]	**0.20 ± 0.05***	**0.18 ± 0.01**			**0.91 ± 0.05***	
Ibuprofen	**0.20 ± 0.01**[f]	**0.22 ± 0.01***	**0.20 ± 0.01**			**0.89 ± 0.04***	
Indometacin	**0.25 ± 0.01**[g]	**0.26 ± 0.02***	**0.25 ± 0.02**			**0.96 ± 0.08***	
Cresolphthalein-dimethylether	**0.31**[a]	**0.32 ± 0.07***	**0.28 ± 0.02**			**0.88 ± 0.10***	
Polyvinylacetate	**0.25**[a]	**0.26 ± 0.01***	**0.25 ± 0.01**			**0.96 ± 0.03***	2.20[h]
N,N-dimethyl-3-methylbenzamide		0.16 ± 0.01	0.15 ± 0.01			**0.98 ± 0.03***	

[a]From Ref. 50.
[b]From Ref. 49.
[c]From Ref. 51.
[d]From Ref. 52.
[e]From Ref. 55.
[f]From Ref. 53.
[g]From Ref. 54.
[h]From Ref. 56.

based on the classical Ehrenfest equations agree with the results of the analysis of experimental measurements for only one of the six studied materials, which shows that the classical Prigogine-Defay ratio Π is mostly not satisfied for the analyzed glass formers.

It should be mentioned that many results of computer simulations of molecular dynamics confirmed the connection between γ and the effective exponent used to model the repulsive part of intermolecular potential.[57–64] For dense systems, the physically relevant intermolecular potential can be successfully approximated by the effective potential, which consists of a dominating part describing repulsive interactions (proportional to the power of the intermolecular distance, $r^{-3\gamma}$) and nearly constant small background, reflecting attractive forces. Thus, in a limiting case, when $\gamma \to 0$, molecular dynamics of dense systems is controlled only by thermal energy fluctuations and the glass transition occurs at constant temperature independently of pressure. In this case, $dT_g/dp = 0$, which one obtains from Eqs. (3) and (4) when $\gamma \to 0$. Then, Π_{GT} equals $\sqrt{\Delta C_p/\Delta C_v}$. In the second limiting case, when molecular dynamics is governed only by volume (for the free volume model, $\gamma \to \infty$, which follows from the effective potential in case of the hard sphere model), Eq. (4) becomes identical with the expression, $dT_g/dp = \kappa_T/\alpha_p$, recently proposed by J. W. P. Schmeltzer also for "free volume model."[10] In this case, Eq. (3) turns into $dT_g/dp = \sqrt{vT_g\kappa_T/\Delta C_p}$, and hence, $\Pi_{GT} = \sqrt{\kappa_T \Delta C_p T_g^{-1} v^{-1} \alpha_p^{-2}}$, becoming similar to the root of the classical Prigogine-Defay ratio.

V. SUMMARY AND CONCLUSIONS

In this paper, we derived the new equation for the pressure coefficient of the glass transition temperature, the predictions of which are very consistent with the results of direct analysis of experimental measurements for many different glass formers. Our new equation is derived in terms of the linear dependence of $\log T_g$ on $\log v_g$ and the approximation proposed by Berthier *et al.*[34,35] for the relationship among the degrees of the dynamic heterogeneity. Moreover, combining this new equation for dT_g/dp and another expression recently proposed by us[49] also for dT_g/dp, we established the new relationship among thermodynamic coefficients at the glass transition Π_{GT}. Experimentally verifying Π_{GT}, we confirmed that its values are consistent with theoretical expectations for all the examined glass formers. It is worth noting that we tested materials, which belong to different material groups such as van der Waals liquids, polymers, ionic liquids, and hydrogen bonded liquids. Thus, we can claim that Π_{GT} correctly describes the relationship among thermodynamic coefficients at the glass transition, for which suitable form of aforementioned relation has been sought after since 1950s when the well-known Prigogine-Defay ratio turned out to be incorrect at the liquid-glass transition.

ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Polish National Science Center based on Decision No.

DEC-2012/04/A/ST3/00337 within the Program No. MAESTRO 2.

[1]M. Paluch, S. Hensel-Bielowka, and T. Psurek, J. Chem. Phys. **113**, 4374 (2000).
[2]M. Paluch, J. Chem. Phys. **115**, 10029 (2001).
[3]S. Hensel-Bielowka, J. Ziolo, M. Paluch, and C. M. Roland, J. Chem. Phys. **117**, 2317 (2002).
[4]R. Casalini, M. Paluch, J. J. Fontanella, and C. M. Roland, J. Chem. Phys. **117**, 4901 (2002).
[5]R. Casalini, M. Paluch, and C. M. Roland, J. Phys. Chem. A **107**, 2369 (2003).
[6]S. Pawlus, M. Paluch, J. Ziolo, and C. M. Roland, J. Phys.: Condens. Matter **21**, 332101 (2009).
[7]M. Paluch, S. Pawlus, A. Grzybowski, K. Grzybowska, P. Wlodarczyk, and J. Ziolo, Phys. Rev. E **84**, 052501 (2011).
[8]I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans Green, New York, 1954), Chap. 9.
[9]N. Hirai and H. Eyring, J. Polym. Sci. **37**, 51 (1959).
[10]J. W. P. Schmelzer, J. Chem. Phys. **136**, 074512 (2012).
[11]*The Glass Transition and the Nature of the Glassy State*, edited by M. Goldstein and R. Simha (Annals New York Academy of Sciences, New York, 1976), Vol. 279.
[12]C. A. Angell and W. Sichina, Ann. N. Y. Acad. Sci. **279**, 53 (1976).
[13]R. O. Davies and G. O. Jones, Proc. R. Soc. A **217**, 26 (1953).
[14]H.-J. Oels and G. Rehage, Macromolecules **10**, 1036 (1977).
[15]M. Goldstein, J. Phys. Chem. **77**, 667 (1973).
[16]M. Goldstein, J. Chem. Phys. **39**, 3369 (1963).
[17]R. O. Davies and G. O. Jones, Adv. Phys. **2**, 370 (1953).
[18]J. M. O'Reilly, J. Polym. Sci. **57**, 429 (1962).
[19]U. Bianchi, J. Phys. Chem. **69**, 1497 (1965).
[20]E. N. Dalal and P. J. Phillips, Macromolecules **16**, 890 (1983).
[21]M. Naoki, K. Matsumoto, and M. Matsushita, J. Phys. Chem. **90**, 4423 (1986).
[22]S. Ichihara, A. Komatsu, Y. Tsujita, T. Nose, and T. Hata, Polym. J. **2**, 530 (1971).
[23]Th. M. Nieuwenhuizen, Phys. Rev. Lett. **79**, 1317 (1997).
[24]A. Grzybowski, K. Grzybowska, M. Paluch, A. Swiety, and K. Koperwas, Phys. Rev. E **83**, 041505 (2011).
[25]I. M. Hodge, J. Non-Cryst. Solids **169**, 211 (1994).
[26]See supplementary material at http://dx.doi.org/10.1063/1.4923005 for details of analysis of examined materials and theoretical basis for estimation of the degree of the dynamic heterogeneity.
[27]G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[28]M. D. Ediger, Annu. Rev. Phys. Chem. **51**, 99 (2000).
[29]R. Richert, J. Phys.: Condens. Matter **14**, R703 (2002).
[30]G. Williams, J. Non-Cryst. Solids **131**, 1 (1991).
[31]K. L. Ngai, J. Non-Cryst. Solids **257**, 7 (2000).
[32]S. A. Mackowiak, T. Herman, and L. J. Kaufman, J. Chem. Phys. **131**, 244513 (2009).
[33]L. M. Leone and L. J. Kaufman, J. Chem. Phys. **138**, 12A524 (2013).
[34]C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hôte, and G. Tarjus, Phys. Rev. E **76**, 041510 (2007).
[35]L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pierno, Science **310**, 1797 (2005).
[36]C. Crauste-Thibierge, C. Brun, F. Ladieu, D. L'Hôte, G. Biroli, and J.-P. Bouchaud, Phys. Rev. Lett. **104**, 165703 (2010).
[37]Th. Bauer, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **111**, 225702 (2013).
[38]A. R. Abate and D. J. Durian, Phys. Rev. E **76**, 021306 (2007).
[39]Z. Rotman and E. Eisenberg, Phys. Rev. Lett. **105**, 225503 (2010).
[40]R. Casalini, D. Fragiadakis, and C. M. Roland, J. Chem. Phys. **142**, 064504 (2015).
[41]C. M. Roland, D. Fragiadakis, D. Coslovich, S. Capaccioli, and K. L. Ngai, J. Chem. Phys. **133**, 124507 (2010).
[42]D. Fragiadakis, R. Casalini, and C. M. Roland, Phys. Rev. E **84**, 042501 (2011).
[43]A. Grzybowski, K. Kołodziejczyk, K. Koperwas, K. Grzybowska, and M. Paluch, Phys. Rev. B **85**, 220201(R) (2012).
[44]K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, and M. Paluch, J. Non-Cryst. Solids **407**, 196 (2015).
[45]S. Capaccioli, G. Ruocco, and F. Zamponi, J. Phys. Chem. B **112**, 10652 (2008).
[46]K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, A. P. Sokolov, and M. Paluch, Phys. Rev. Lett. **111**, 125701 (2013).
[47]S. Pawlus, M. Paluch, and A. Grzybowski, J. Chem. Phys. **134**, 041103 (2011).
[48]M. Paluch, E. Masiewicz, A. Grzybowski, S. Pawlus, J. Pionteck, and Z. Wojnarowska, J. Chem. Phys. **141**, 134507 (2014).
[49]K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, J. Pionteck, A. P. Sokolov, and M. Paluch, Phys. Rev. E **86**, 041502 (2012).
[50]C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. **68**, 1405 (2005).
[51]Z. Wojnarowska, M. Paluch, A. Grzybowski, K. Adrjanowicz, K. Grzybowska, K. Kaminski, P. Wlodarczyk, and J. Pionteck, J. Chem. Phys. **131**, 104505 (2009).
[52]S. Takahara, M. Ishikawa, O. Yamamuro, and T. Matsuo, J. Phys. Chem. B **103**, 792 (1999).
[53]K. Adrjanowicz, K. Kaminski, Z. Wojnarowska, M. Dulski, L. Hawelek, S. Pawlus, W. Sawicki, and M. Paluch, J. Phys. Chem. B **114**, 6579 (2010).
[54]Z. Wojnarowska, K. Adrjanowicz, P. Wlodarczyk, E. Kaminska, K. Kaminski, K. Grzybowska, R. Wrzalik, M. Paluch, and K. L. Ngai, J. Phys. Chem. B **113**, 12536 (2009).
[55]D. Gundermann, U. R. Pedersen, T. Hecksher, N. P. Bailey, B. Jakobsen, T. Christensen, N. B. Olsen, T. B. Schrøder, D. Fragiadakis, R. Casalini, C. M. Roland, J. C. Dyre, and K. Niss, Nat. Phys. **7**, 816 (2011).
[56]P. K. Gupta and C. T. Moyanihan, J. Chem. Phys. **65**, 4136 (1976).
[57]C. M. Roland, S. Bair, and R. Casalini, J. Chem. Phys. **152**, 124508 (2006).
[58]U. R. Pedersen, N. P. Bailey, T. B. Schrøder, and J. C. Dyre, Phys. Rev. Lett. **100**, 015701 (2008).
[59]N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schrøder, and J. C. Dyre, J. Chem. Phys. **129**, 184507 (2008).
[60]N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schrøder, and J. C. Dyre, J. Chem. Phys. **129**, 184508 (2008).
[61]D. Coslovich and C. M. Roland, J. Phys. Chem. B **112**, 1329 (2008).
[62]D. Coslovich and C. M. Roland, J. Chem. Phys. **130**, 014508 (2009).
[63]T. B. Schrøder, U. R. Pedersen, N. P. Bailey, S. Toxvaerd, and J. C. Dyre, Phys. Rev. E **80**, 041502 (2009).
[64]A. Grzybowski, K. Koperwas, and M. Paluch, Phys. Rev. E **86**, 031501 (2012).

4.3. W POSZUKIWANIU KORELACJI POMIĘDZY CZTEROPUNKTOWĄ MIARĄ DYNAMICZNEJ HETEROGENICZNOŚCI A INNYMI CHARAKTERYSTYKAMI CIECZY FORMUJĄCYCH SZKŁA W WARUNKACH PODWYŻSZONEGO CIŚNIENIA

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Referencja: J. Non-Cryst. Sol. 407, 196 (2015)

Skrót:

W artykule sprawdzamy sugerowane liniowe korelacje pomiędzy czteropunktową dynamiczną heterogenicznością a objętością aktywacji oraz różnicą pomiędzy izobaryczną i izochoryczną kruchością, które były testowane głównie w ciśnieniu atmosferycznym dla różnych materiałów w pobliżu przejścia szklistego. Nasza analiza została przeprowadzona dla dwunastu materiałów należących do różnych grup materiałowych, takich jak: ciecze van der Waalsa, polimery, protonowe ciecze jonowe, ciecze z wiązaniami wodorowymi. Ponieważ ostatnie badania [Phys. Rev. Lett. 111 (2013) 125701] pokazują, że dynamiczna heterogeniczność maleje wraz ze wzrostem ciśnienia w warunkach przejścia szklistego, co pozostaje w sprzeczności z niezmienniczością kształtu izochronicznych widm dielektrycznych, wykorzystujemy ciśnieniowe dane eksperymentalne do zbadania czy analizowane korelacje wystąpią wcałej przestrzeni diagramu fazowego właściwej cieczom przechłodzonym. Otrzymane wyniki są teoretycznie wyjaśnione za pomocą zaproponowanych przez Berthiera i współautorów [Science 310 (2005) 1797] estymat stopnia dynamicznej heterogeniczności.

Journal of Non-Crystalline Solids 407 (2015) 196–205

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

In search of correlations between the four-point measure of dynamic heterogeneity and other characteristics of glass-forming liquids under high pressure

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ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form 21 July 2014
Available online 10 August 2014

Keywords:
Dynamic heterogeneity of glass-forming liquids;
Four-point dynamic susceptibility;
Dynamic length scale and time scale of molecular dynamics near the glass transition;
Activation volume of glass-forming liquids;
Fragility of glass-forming liquids in isobaric and isochoric conditions

ABSTRACT

In this paper, we examine the linear correlations earlier suggested between the four-point dynamic heterogeneity and the activation volume as well as between the four-point dynamic heterogeneity and the difference between isobaric and isochoric fragilities, which have been previously tested mainly at ambient pressure for different materials near the glass transition. We perform our analyses for twelve glass formers that belong to different material groups such as van der Waals liquids, polymer melts, protic ionic liquids, and strongly hydrogen-bonded liquids. Since our very recent finding [Phys. Rev. Lett. 111 (2013) 125701] shows that the dynamic heterogeneity decreases with increasing pressure along the glass transition line in the phase diagram, which is in contrast to the invariance of the shape of relaxation spectra in isochronal conditions, we exploit experimental data measured at ambient and elevated pressure to test whether the correlations occur over the whole phase diagram area where the supercooled liquid state is achieved. The obtained results are clarified theoretically in the limit of the estimate recently proposed for the degree of the dynamic heterogeneity by Berthier et al. [Science 310 (2005) 1797].

1. Introduction

Close to the glass transition, materials become denser, distances between molecules decrease and molecular motions are more dependent on each other. This molecular behavior of supercooled liquids leads to the drastic growth of their viscosity η and their structural relaxation time τ in a relatively small temperature range. It makes a complete understanding of the glass transition mechanism one of the most interesting problems in the condensed matter physics. Since supercooled liquids become denser when they are approaching the glass transition, their molecular packing increases, and consequently their molecular rearrangements become cooperative, which was suggested by Adam and Gibbs [1] already in 1965. The authors introduced an idea of cooperative rearranging regions (CRR), within which molecular motions depend on each other. Recent works have shown that sizes of the regions do not have to be constant in time and space [2–4], thus the dynamics of molecules, which belong to different regions, is not identical even if the macroscopic structural relaxation time τ remains unchanged. It implies that the molecular dynamics of supercooled liquids becomes heterogeneous [5–20]. The introduction of the concept of the dynamic heterogeneity enhances our understanding of the liquid-glass transition and related phenomena, because it describes the situation at which molecules expose different dynamic properties (as a function of time and/or space), although they belong to the same system at a given thermodynamic state. It has been suggested that the broadening of the dielectric relaxation spectra, which is usually observed in the dielectric spectroscopy experiments when the examined sample is approaching the glass transition can be related to the molecular dynamics diversity [9,21,22]. However, it has been recently shown that the dynamic heterogeneity in isochronal conditions is not constant but it usually decreases with increasing pressure p or temperature T [23–26], although the structural relaxation spectrum remains unchanged at $\tau = const.$ [27], which is in accord with the results earlier obtained from boson peak experiments [3]. This important finding requires our understanding of the connection between the dynamic heterogeneity and the stretching of the structural relaxation peak. Thus, the further study of the influence of thermodynamic conditions on the structural relaxation times, with respect to the dynamic heterogeneity, should enable us to gain a better insight into the molecular dynamics near the glass transition. The sensitivity of the relaxation times to changes in p and T can be characterized respectively by the activation volume v_{act} and the fragility parameters (the isobaric one m_p or the isochoric one m_v). Sokolov et al. [2–4] earlier studied the characteristic dynamic correlation length scale ξ determined from so-called boson peak experiments (it should be noted here that the microscopic nature of boson peak is still discussed, but many researchers relate it to some characteristic correlation or heterogeneity length in disordered structure [28–32], e.g., to the characteristic correlation length of fluctuations in elastic constants [28,32])

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http://dx.doi.org/10.1016/j.jnoncrysol.2014.07.033
0022-3093/

and they suggested common correlations in double logarithmic scale between ξ and v_{act} as well as between ξ and $m_p - m_v$ for various molecular, hydrogen-bonding and polymeric glass formers.

In this work, we make further progress in our understanding of the connection between the structural relaxation and the dynamic heterogeneity by thorough examinations of the suggested correlations in wide pressure ranges for twelve materials that belong to different material groups such as van der Walls liquids, polymer melts, protic ionic liquids, and strongly hydrogen-bonded liquids.

2. Method

In supercooled liquids, as already mentioned, there are regions of different dynamics, which are characterized by the length scale of the dynamic heterogeneity, ξ. The length scale ξ can be interpreted as their size, e.g. if we assume that the above regions are cubic the length scale of the dynamic heterogeneity is a length of their edge and their volume in molecular units can be obtained by $\chi_4^{max} \cong (\xi/a)^{\varsigma}$ [15], where χ_4^{max} is a maximum of four-point time-dependent correlation function $\chi_4(t)$ called the dynamic susceptibility, a is a molecular size. Although the cubic shape of the regions is often assumed (i.e., $\zeta = 3$), the value of exponent ζ falls between 2 and 4 according to numerical [10,33] and theoretical [8,14,33,34] investigations. The above relation connects ξ and the maximum of the dynamic susceptibility function. The latter has been acknowledged as a good measure of the degree of the dynamic heterogeneity [10,15,33,35–38], which is directly related to the characteristic correlation volume (i.e., a typical volume of regions of dynamically correlated molecules) or the average number of dynamically correlated molecules [8,10,14,15,36,37,39]. Moreover, the connection between the length scale of the dynamic heterogeneity and the maximum of the dynamic susceptibility function implies that the correlations suggested by Sokolov et al. [2–4], which can be transformed to the following linear dependences: log ξ(log v_{act}) and log ξ (log($m_p - m_v$)), should also be observed between log χ_4^{max} and log v_{act} or between log χ_4^{max} and log($m_p - m_v$). The direct experimental measurements of the function $\chi_4(t)$ require detecting a nonlinear response of examined samples, which is not accessible in standard spectroscopy methods. However, such standard relaxation experiments, which enable to detect a linear response of supercooled liquids, can provide useful information about the degree of the dynamic heterogeneity. The ensemble-average two-point correlators $C(t, 0) = \delta O(t)\delta O(0)$, where δO is the instantaneous value of the fluctuations of some observable O (e.g., density) relative to its ensemble average $\langle O\rangle$, can be used. Although a direct measurement of spontaneous fluctuations of dynamic correlators is very complex, it is still possible to analyze induced fluctuations using a derivative function $\chi_n(t) = \partial\langle C(t, 0)\rangle/\partial n$, where $\langle\rangle$ means an ensemble average of $C(t, 0)$ and n is a quantity which triggers fluctuations that contribute to the dynamic heterogeneity. Berthier et al. [15,39] analyzed the dynamic susceptibility in the *NPT* ensemble by exploiting the formalism, which was based on a linear response of measured system and they obtained a direct relation between $\chi_4(t)$ and $\chi_n(t)$: $\chi_4^{NPT}(t) = \frac{k_B}{\Delta c_p} T^2 \left(\chi_T^{NPT}(t)\right)^2 + \chi_4^{NPH}(t)$, where T is a temperature, k_B is the Boltzmann constant, Δc_p is a difference between the isobaric heat capacities of liquid and glassy states, $\chi_T^{NPT}(t)$ is the dynamic susceptibility that is induced by temperature fluctuations and $\chi_4^{NPH}(t)$ quantifies the amplitude of $C(t, 0)$ in the *NPH* ensemble in which all configurations have the same enthalpy. It has been argued that $\chi_4^{NPH}(t)$ is expected to be a small positive number [39–41], therefore the term $\chi_4^{NPH}(t)$ can be neglected. The use of configurational values of the heat capacity, Δc_p, minimalizes the effect of fluctuations unrelated with glassy state, which may contribute to the heat capacity of real materials [15]. It is worth noting that non-configurational values of the heat capacity give qualitatively the same dependences of the degree of the dynamic heterogeneity on pressure and temperature at a constant relaxation time, but then the estimated relative contribution to the degree of the dynamic heterogeneity induced by the temperature and the density fluctuations turns out to be unphysical, therefore the use of Δc_p is proper in the case of real materials instead of c_p [23]. By assuming that two-point linear correlation function can be parameterized by Kohlrausch–Williams–Watts (KWW) function $\Phi(t) = \exp[-(t/\tau)^{\beta}]$, one can arrive at the following expression for the maximum of the dynamic susceptibility function:

$$(\chi_4)^{max} \approx \frac{k_B T^2}{\Delta c_p}\left(\frac{\beta}{e}\frac{\partial \ln\tau}{\partial T}\Big|_p\right)^2, \quad (1)$$

where β is a stretching exponent. We have to stress that some points of estimating the degree of the dynamic heterogeneity by Eq. (1) are still fervently discussed [42,43], however, this approach has been successfully tested for van der Waals liquids [24]. Moreover, there is a consensus that this approach remains a good estimate of the degree of the dynamic heterogeneity for many other systems [12,15,23–26,39], thus we use it to study several glass-formers, which belong to different material groups such as van der Walls liquids, polymer melts, protic ionic liquids, and strongly hydrogen-bonded liquids. To better clarify the origin of the estimate of the height of the peak of the four point dynamic susceptibility, which is given by Eq. (1), it should be noted that it follows from the approximation $(\chi_4)^{max} \approx k_B T^2(\chi_T(\tau))^2/\Delta c_p$, where $\chi_T(\tau) = (\partial\Phi(t)/\partial t)_p|_{t=\tau}$ is calculated in the NPT ensemble, i.e., $\chi_T(t) = \chi_T^{NPT}(t)$, and $\Phi(t) = \exp[-(t/\tau)^{\beta}]$.

The evaluation of the degree of the dynamic heterogeneity by Eq. (1) requires quantifying the functions $\Delta c_p(T, p)$, $\tau(T, p)$, and $\beta(T, p)$. The isobaric heat capacity data for glibenclamide (GLB) (also reported in Ref. [23]), verapamil hydrochloride (VH), carvedilol base (CB), N,N-diethyl-3-methylbenzamide (DEET), ibuprofen (IBP), indometacin (IND), and dipropylene glycol (DPG), have been measured at ambient pressure by us using the differential scanning calorimetry with stochastic temperature modulation (TOPEM), whereas literature reports on $c_p(T)$ at $p = 0.1$ MPa for 1,1′-bis (p-methoxyphenyl) cyclohexane (BMPC) [44],cresol-phthalein-dimethylether (KDE) [44], phenolphthalein-dimethylether (PDE) [44], ortho-Terphenyl (OTP) [45], polyvinylacetate (PVAc) [46] have been exploited. Based on the temperature dependence of the isobaric heat capacity data measured at ambient pressure, we have estimated the temperature and the pressure dependence of Δc_p in the way already employed in our previous papers devoted to the four-point measure of the dynamic heterogeneity [23–25], i.e., calculating the difference between the heat capacities in the liquid and glassy states at ambient pressure $\Delta c_p(T, p_0) = c_p^{liquid}(T, p_0) - c_p^{glass}(T, p_0)$ on the assumption that the heat capacity in the glassy state is nearly constant and equal to its value at the glass transition temperature T_g at ambient pressure, $c_p^{glass}(T, p_0) \approx c_p^{glass}(T_g, p_0)$, and then evaluating Δc_p at different temperatures and pressures based on Maxwell's thermodynamic relations as follows, $\Delta c_p(T, p) = \Delta c_p(T, p_0) + T\int_{p_0}^{p}\left(\frac{\partial^2 v}{\partial T^2}\right)dp$, where the dependence $v(T, p)$ has to be exploited. To do that we use one of the equations of state (EOS), which have been derived by us [47–52] for viscous liquids. This EOS very successfully describes the dependence of volume on pressure and temperature for studied materials, using values of the EOS parameters (Eq. (9) in [47]) either earlier reported (for BMPC [24], GLB [53], OTP [54], PDE [47], PVAc [47], DPG [55], and VH [55]) or found here by fitting PVT experimental data of KDE, DEET, IBP, CB, and IND to the EOS (see Table 1). We need to stress that the density–temperature ranges explored in our analyses do not require implementing our newest equations of state very recently derived [52] for the extremely wide range of volumetric data, which should be applied to properly describe all volumetric properties of liquids measured in the extremely density–temperature range as has been very recently shown by us [56] for the thermal isobaric volume expansivity directly obtained from the scanning transitiometry experiment. Thus, the PVT experimental data measured

Table 1
The values of the fitting parameters of the equation of state, $v(T,p) = \left[A_0 + A_1(T-T_0) + A_2(T-T_0)^2\right]\left[1 + (p-p_0)\gamma_{EOS}\exp(b_2(T-T_0)/B_{T_0}(p_0)\right]^{-1/\gamma_{EOS}}$ (derived in [47] as Eq. (9)), for analyzed materials, which have been obtained assuming a fixed reference state (T_0, p_0) where $p_0 = 0.1$ MPa for all materials except for IND, for which $p_0 = 0$ MPa. Adjusted coefficients of determination (adj.-R^2) show the high quality of the fits.

Material	$T_0[K]$	$A_0[cm^3/g]$	$A_1[cm^3/(g \cdot K)]$	$A_2[cm^3/(g \cdot K^2)]$	$B_{T_0}(p_0)[MPa]$	$b_2[K^{-1}]$	γ_{EOS}	Adj.-R^2
KDE	314.50	0.7725 ± 0.0001	$(4.93 \pm 0.03)\cdot10^{-4}$	$(5.94 \pm 0.05)\cdot10^{-7}$	2512 ± 9	$(4.74 \pm 0.04)\cdot10^{-3}$	9.74 ± 0.06	0.99991
DEET	197.20	0.9371 ± 0.0002	$(5.87 \pm 0.04)\cdot10^{-4}$	$(5.12 \pm 0.15)\cdot10^{-7}$	3785 ± 9	$(5.60 \pm 0.02)\cdot10^{-3}$	10.98 ± 0.03	0.99995
IBP	273.00	0.9760 ± 0.0004	$(7.58 \pm 0.12)\cdot10^{-4}$	$(6.25 \pm 0.15)\cdot10^{-7}$	2041 ± 11	$(5.89 \pm 0.06)\cdot10^{-3}$	11.15 ± 0.06	0.99990
CB	273.15	0.7983 ± 0.0002	$(5.32 \pm 0.05)\cdot10^{-4}$	$(2.52 \pm 0.72)\cdot10^{-8}$	3772 ± 19	$(4.06 \pm 0.05)\cdot10^{-3}$	10.07 ± 0.10	0.99992
IND	273.00	0.7464 ± 0.0009	$(4.02 \pm 0.25)\cdot10^{-4}$	$(4.02 \pm 1.73)\cdot10^{-8}$	3357 ± 79	$(4.76 \pm 0.30)\cdot10^{-3}$	13.21 ± 0.25	0.99977

typically up to the pressure of 200 MPa and their accurate fits to the equation of state derived as Eq. (9) in [47] have been proper to find the reliable density–temperature dependences of the structural relaxation times. Consequently, the structural relaxation times employed in Eq. (1) have been accurately determined by using the temperature–volume version [57] of the Avramov entropic model [58] with values of the model parameters collected in Table 2, which have been found from fitting experimental dependences $\tau(T, v)$ to the model. The dependences $\tau(T, v)$ have been obtained from isobaric and isothermal broadband dielectric measurements (the results of which have been earlier reported for all examined materials as follows BMPC [59], GLB [60], OTP [61], PDE [57], KDE [62], PVAc [63], VH [64], DEET [65], IBP [66], CB [67], IND [68], and DPG [69, 70]) and the mentioned EOS that has enabled to transform the original dependence $\tau(T, p)$ to $\tau(T, v)$. For reliability of our analyses, it is also important that the pressure ranges explored in our analyses based on Eq. (1), which are explicitly shown in the caption of Fig. 3, match or only slightly exceed the experimental pressure ranges within which dielectric data have been measured. Since we have observed in the case of each studied supercooled liquid that the structural dielectric relaxation peaks at a given relaxation time possess the same shape for different (T, p) pairs in the measurement range, we treat the parameter β as a function of only τ, similarly as we have done in Refs. [23–25].

To obtain the value of the activation volume one can use the well-known formula,

$$v_{act} \cong RT\left(\frac{d\ln\tau}{dp}\right)_T, \tag{2}$$

which defines v_{act} in isothermal conditions. However, the value of v_{act} depends also on temperature and there is a relation between the activation volume and the measure of the sensitivity of molecular dynamics to changes in temperature, which is the isobaric fragility [71], $v_{act} = m_p R\ ln(10) dT_g/dp$, where dT_g/dp is a pressure coefficient of the glass transition temperature. Thus, the activation volume is a function of temperature and pressure $v_{act}(T, p)$, similarly to the specific volume. Since our analysis are performed in wide ranges of pressures and temperatures, we employed the very recently established equation of state for the activation volume (EOS_{act}) [55], which enables us to calculate the values of the activation volume in any thermodynamic conditions:

$$v_{act}(T,p) = \frac{F_0 + F_1(T-T_0) + F_2(T-T_0)^2}{\left[1 + (p-p_0)\frac{\gamma_{act}}{B_{act}(T_0,p_0)}\exp[g_2(T-T_0)]\right]^{1/\gamma_{act}}}, \tag{3}$$

where $F_0 = v_{act}(T_0,p_0)$, $F_1 = \partial v_{act}(T,p_0)/\partial T|_{T=T_0}$, $F_2 = \frac{1}{2}\partial^2 v_{act}(T,p_0)/\partial T^2|_{T=T_0}$, $g_2 = -\partial \ln B_{act}(T,p_0)/\partial T|_{T=T_0}$, the isothermal bulk modulus for the activation volume at the reference state $B_{act}(T_0,p_0)$, and γ_{act} are fitting parameters, which in general depend on the chosen reference state (T_0,p_0) and the thermodynamic phase (i.e., they can be different for instance for liquid and glassy states), and only the exponent γ_{act} is expected to be a material constant independent of thermodynamic conditions. In our analyses, the reference state is chosen as follows p_0 is the atmospheric pressure and the value of T_0 is fixed at the glass transition temperature at p_0. The EOS_{act} was successfully tested for many materials and the appropriate values of the EOS_{act} parameters have been earlier reported [55] for BMPC, PVAc, VH, PDE, and DPG. The values of fitting parameters for the equation of state for the activation volume obtained here for GLB, OTP, KDE, DEET, IBP, IND, and CB are collected in Table 3. It is worth noting that the use of Eq. (3) with known values of its fitting parameters is a convenient way to evaluate the activation volume values at different temperatures and pressures. As shown in [55] and Table 3, the high quality of the fits to Eq. (3) is confirmed by large values of the adjusted coefficients of determination (adj.-R^2). It should be stressed that the values of the activation volume applied to find the values of the fitting parameters of Eq. (3) have been calculated based on the definition Eq. (2) in the very accurate way described in [55], which relies on all points of the dependences $\tau(T, p)$ determined from the experimental dielectric data for a given material. Additionally, in the analyses reported herein for all materials, we exploit the temperature–pressure experimental ranges explored by the dielectric measurements of the materials, which in some cases are only slightly extended to reach the glass transition line defined at $\tau =$ 100 s. Therefore, the dependences $v_{act}(T, p)$ found from Eq. (3) can be considered as very good approximations of the dependences determined from the experimental data according to the definition given by Eq. (2).

As an example, we illustrate our typical way of fitting dielectric and volumetric data for KDE, for which dielectric data have been collected [62] only at ambient pressure and along an isotherm at T = 364.6 K. It should be noted that only the dielectric data for DPG, for which the standard power law density scaling is unconditionally invalid [74,75], has required more complex fitting [55]. In other cases, in which the power law density scaling is obeyed at least to a good approximation, we have transformed (see Fig. 1(a)–(c)) the temperature–pressure dependences $\tau(T, p)$ determined from isobaric and isothermal dielectric measurements to the corresponding temperature–volume dependences $\tau(T, v)$ using the equation of state (derived as Eq. (9) in [47]) with the values of its parameters obtained from fitting PVT experimental data to the EOS. Then, we have evaluated the activation volume values based on the definition Eq. (2) with $\tau(T, p) = \tau(T, v(T, p))$ at each thermodynamic state (T, p) at which dielectric measurements were carried out for a given material. Although the latter procedure can be also followed to find $v_{act}(T, p)$ at any thermodynamic state point near the glass transition, only the values of $v_{act}(T, p)$ determined

Table 2
The exploited values of the parameters of the temperature–volume version of the Avramov model [57], $\tau = \tau_0 \exp[(AT^{-1}v^{-\gamma})^D]$, for analyzed materials except for DPG, the molecular dynamics of which does not obey the power law density scaling and one set of values of the Avramov model parameters is not sufficient to describe all experimental dependences $\tau = \tau(T, v)$.

Material	$\log_{10}(\tau_0/s)$	$A\ [cm^{3\gamma}g^{-\gamma}K]$	D	γ
BMPC	−12.28 ± 0.10	505 ± 12	2.05 ± 0.03	8.00 ± 0.08
GLB	−8.29 ± 0.23	349 ± 9	5.21 ± 0.21	3.07 ± 0.04
OTP	−12.39 ± 1.02	438 ± 63	3.18 ± 0.36	4.40 ± 0.03
PDE	−9.40 ± 0.04	156 ± 2	4.25 ± 0.04	4.42 ± 0.02
KDE	−11.25 ± 0.13	329 ± 7	2.93 ± 0.05	4.28 ± 0.02
PVAc	−9.01 ± 0.08	409 ± 5	4.85 ± 0.08	2.36 ± 0.02
VH	−9.61 ± 0.08	440 ± 4	4.79 ± 0.06	2.55 ± 0.01
DEET	−9.95 ± 0.09	354 ± 5	3.74 ± 0.05	4.65 ± 0.01
IBP	−8.92 ± 0.27	356 ± 11	4.61 ± 0.18	3.99 ± 0.02
CB	−8.76 ± 0.05	295 ± 1	7.00 ± 0.08	2.50 ± 0.01
IND	−8.51 ± 1.33	219 ± 26	5.54 ± 0.93	3.53 ± 0.03

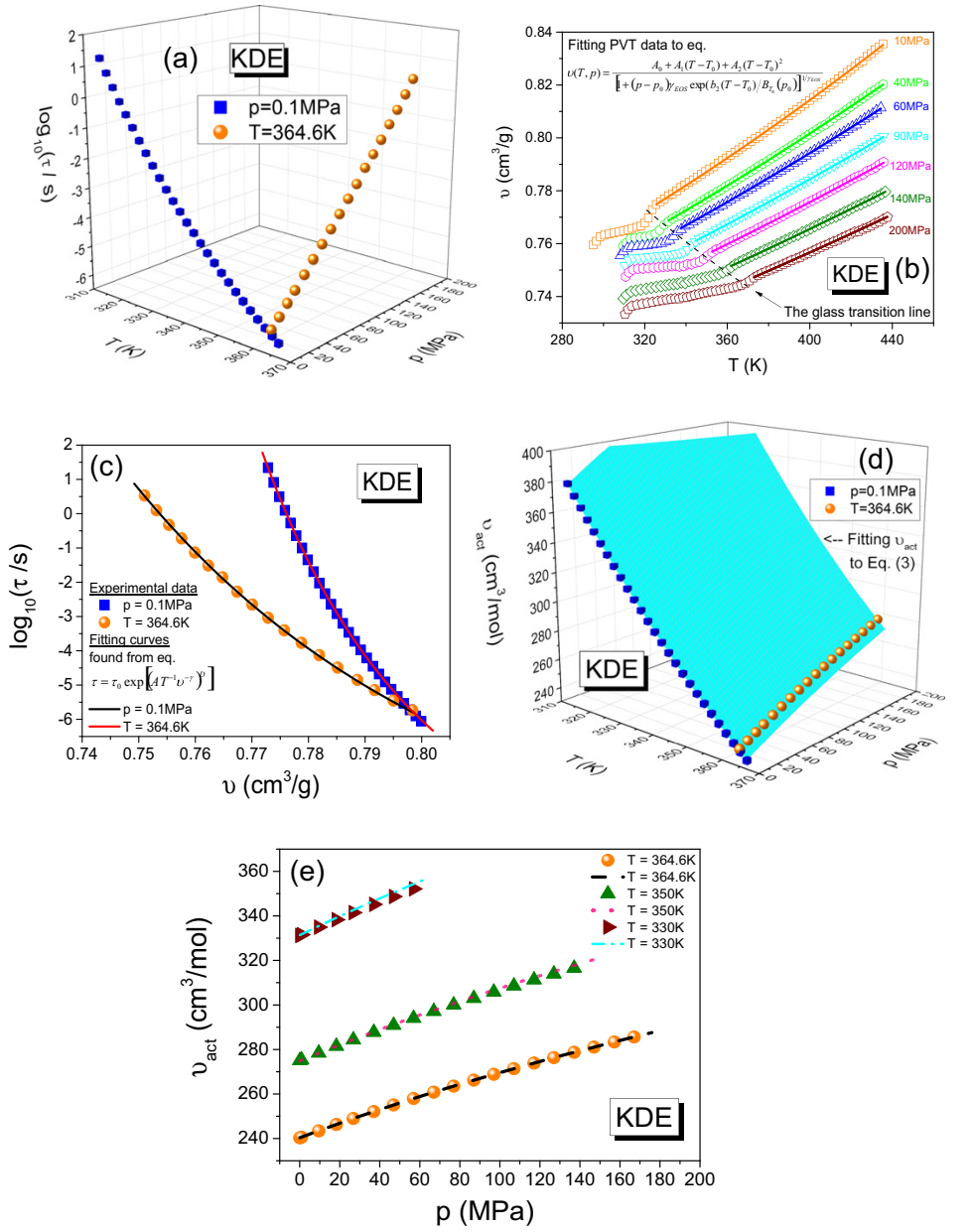

Fig. 1. Illustration of the fitting procedure typically followed for volumetric and dielectric data using measurement data of KDE as an example. (a) Plot of temperature–pressure dependence of structural relaxation times determined directly from measured dielectric loss spectra. (b) Fitting the PVT measurement data to the equation of state derived as Eq. (9) in [47] with values of its parameters collected here in Table 1. Solid lines denote the fitting curves. (c) Fitting the temperature–volume dependences of dielectric structural relaxation time to the temperature–volume version [57] of the Avramov model with values of its parameters collected in Table 2. Solid lines denote the fitting curves. (d) Fitting the temperature–pressure dependences of the activation volume values found from the definition Eq. (2) to the equation of state Eq. (3) with values of its parameters collected in Table 3. The mesh denotes the fitting surface. (e) Comparison of the isothermal pressure dependences obtained from Eqs. (2) and (3) by using an experimental isotherm at T = 364.6 K as well as two generated isotherms at T = 330 K and T = 350 K. Points are determined from Eq. (2) and lines denote the curves generated from Eq. (3).

law density scaling, can exhibit a non-typical behavior of the dynamic heterogeneity with varying thermodynamic conditions at a constant structural relaxation time. Such a hypothesis requires further investigations in the future. However, an explanation of the increase in χ_4^{max} of DPG with increasing pressure in isochronal conditions can be also suggested independently of the density scaling law. Since DPG is a strongly hydrogen-bonded liquid, the increase in pressure increases the number and the strength of the hydrogen-bonds at least up to $p \approx 1$ GPa [70,76], not exceeded in our current analysis for DPG, which implies that the number of dynamically correlated molecules, and thus the degree of the dynamic heterogeneity, rises.

3.2. The degree of the dynamic heterogeneity and the difference between isobaric and isochoric fragilities along the glass transition isochrone

In the previous section, we have shown that there is no general correlation between the degree of the dynamic heterogeneity and the activation volume for all studied materials near the glass transition.

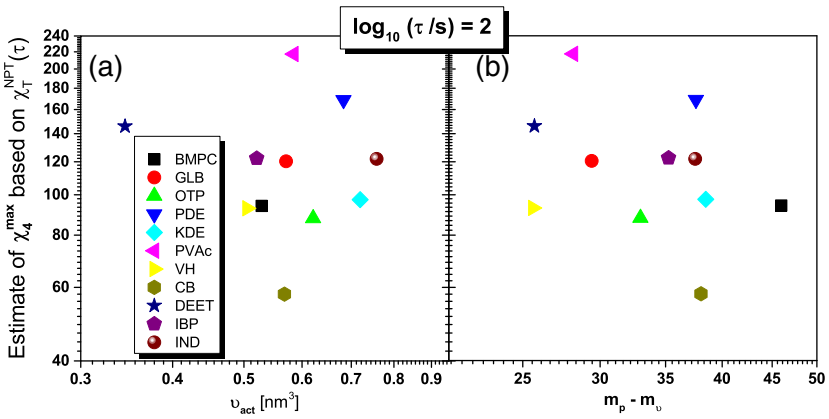

Fig. 2. Plot of the degree of the dynamic heterogeneity vs. the activation volume (a) and the difference between isobaric and isochoric fragilities (b) for all tested materials. The presented results are estimated from Eq. (1) by using experimental data collected at ambient pressure in isochronal conditions ($\tau = 100$ s).

The same conclusion about the correlation between the degree of the dynamic heterogeneity and the difference between isobaric and isochoric fragilities can be drawn from Fig. 4, where the dependences of log χ_4^{max} on log$(m_p - m_\upsilon)$ are presented at $\tau = 100$ s, because each material demonstrates a different behavior of χ_4^{max} when $m_p - m_\upsilon$ changes. As in the case of the correlation tested in the previous section, the linear approximations of the dependence of the logarithm of the degree of the dynamic heterogeneity on the logarithm of the difference between isobaric and isochoric fragilities, which are depicted by dashed straight lines in Fig. 4, are satisfactorily achieved only for some materials. We observe similar results in the figure with axes in linear scales as well. The deviations from the linear dependences, which are especially significant for PVAc, PDE and IND, imply that in general the degree of the dynamic heterogeneity is not any linear function of $m_p - m_\upsilon$ at a constant relaxation time in both the linear and logarithmic scales. Similarly to the effect of pressure on the dependence log χ_4^{max} on log υ_{act}, the increase in pressure causes a deviation of the examined relation between log χ_4^{max} and log$(m_p - m_\upsilon)$ from a linear behavior, but now, the deviation has an opposite curvature than that observed for the dependence log $\chi_4^{max}(log\upsilon_{act})$. As has been noted in the previous section, in the case of DPG, which is the only strongly associated liquid examined herein, the degree of the dynamic heterogeneity increases as pressure increases, therefore the pressure behavior of the dependence of the degree of the dynamic heterogeneity on the difference between isobaric and isochoric fragilities for DPG is opposite to that observed for the other tested materials.

3.3. Theoretical explanations of the high pressure experimental tests

Now, we briefly present the theoretical explanation of the correlation between the dynamic heterogeneity and the activation volume as well as the dynamic heterogeneity and the difference between isobaric and isochoric fragilities. As a starting point to analyze the dependence $\chi_4^{max}(\upsilon_{act})$, we take the complete differential of the logarithm of the structural relaxation time, which is a function of the temperature and the pressure, $d\log\tau = \left(\frac{\partial \log\tau}{\partial T}\right)_p dT + \left(\frac{\partial \log\tau}{\partial p}\right)_T dp = 0$, when $\tau = const$.

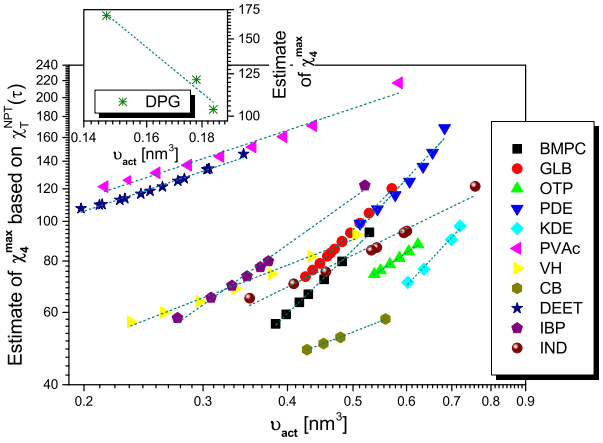

Fig. 3. Plot of the dependences of the degree of the dynamic heterogeneity on the activation volume in isochronal conditions ($\tau = 100$ s). For each material, the values of χ_4^{max} are estimated from Eq. (1) at ambient and elevated pressures respectively up to 215 MPa for BMPC, 190 MPa for GLB, 91 MPa for OTP, 363 MPa for PDE, 137 MPa for KDE, 715 MPa for PVAc, 452 MPa for VH, 170 MPa for CB, 1065 MPa for DEET, 440 MPa for IBP, 395 MPa for IND, and 645 MPa for DPG. The results obtained for DPG are presented in the inset. The dashed lines are only guides for the eyes.

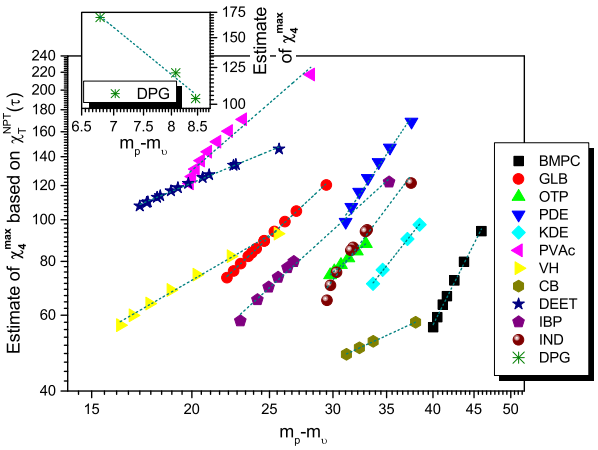

Fig. 4. Plot of the dependences of the degree of the dynamic heterogeneity on the difference between isobaric and isochoric fragilities in isochronal conditions ($\tau = 100$ s). For each material, the values of χ_4^{max} are estimated from Eq. (1) at ambient and elevated pressures in the same ranges as explored in Fig. 3. The results obtained for DPG are presented in the inset. The dashed lines are only guides for the eyes.

Then $0 = \left(\frac{\partial \log\tau}{\partial T}\right)_p + \left(\frac{\partial \log\tau}{\partial p}\right)_T \frac{dp}{dT}$. Exploiting Eqs. (1) and (2), we find the sought after formula:

$$\chi_4^{max} = \upsilon_{act}^2 \frac{\beta_{KWW}^2}{e^2 \Delta C_p R} \left(\frac{dp}{dT}\right)^2 \tag{5a}$$

and after taking its logarithm, we arrive at the following equation

$$\log \chi_4^{max} = 2 \log \upsilon_{act} + 2 \log \frac{1}{\sqrt{\Delta C_p}} \left(\frac{dp}{dT}\right) + 2 \log \frac{\beta_{KWW}}{e\sqrt{R}}. \tag{5b}$$

Along the glass transition line, which can be defined as already mentioned at a constant relaxation time to a good approximation, dT/dp becomes the pressure coefficient of the glass transition temperature. Since the last term of the right side of Eq. (5b) is usually constant, because the stretching parameter β_{KWW} is constant at a constant relaxation time in case of many glass formers, we can observe a linear dependence $\log \chi_4^{max}(\log \upsilon_{act})$ only if $\sqrt{\Delta C_p} dT/dp$ is invariant as pressure increases at $\tau = const.$. In this case, the value of the slope of the possible linear dependence should be equal to 2 according to Eq. (5b) for all materials, and then the one linear correlation should exist However, the evident changes of the values of the middle term of Eq. (5b) in the examined pressure ranges at $\tau = 100$ s are presented in Fig. 5a for two van der Waals liquids (BMPC and GLB) and polymer PVAc. To obtain the dependences of the term $\sqrt{\Delta C_p} dT/dp$ on pressure we used the recently published equation for the pressure coefficient of the glass transition temperature [53], which is also valid at any constant structural relaxation time, $dT_\tau/dp = \gamma T_\tau \kappa_{T_\tau} \left[1 + \gamma T_\tau \alpha_p(T_\tau)\right]^{-1}$. Despite the fact that the changes in the values of the middle term of Eq. (5b) for examined van der Walls liquids with increasing pressure are much smaller than that obtained for the tested polymer, the value of $\sqrt{\Delta C_p} dT/dp$ in general varies as pressure increases, which implies that one general linear dependence $\log \chi_4^{max}(\log \upsilon_{act})$ for all materials does not exist. However, as already mentioned from the inspection of Fig. 3, the logarithms of the degree of the dynamic heterogeneity can be satisfactorily approximated in case of some tested materials by linear functions of the logarithm of the activation volume with different slopes depending on materials. Thus, in these cases, the term $\log(\sqrt{\Delta C_p} dT/dp)$ should be a linear function of the logarithm of the activation volume, $\log(\sqrt{\Delta C_p} dT/dp) = A \log \upsilon_{act} + B$, to a good approximation. Exploiting this assumption, Eq. (5b) transforms to $\log \chi_4^{max} = 2(1 - A)\log \upsilon_{act} + C$, where A and C are constant parameters, and a linear dependence of $\log \chi_4^{max}$ on $\log \upsilon_{act}$ with its slope defined as $2(1 - A)$ can be obtained, where the value of the slope A can be different for different materials as it is suggested by the results presented in Fig. 3. For instance, the dependences of the middle term of the right side of Eq. (5b) on the activation volume shown in Fig. 5b are linear for van der Waals liquids BMPC and GLB, for which the slope $A \approx 0.20$ and 0.15, respectively. Consequently, the dependence $\log \chi_4^{max}(\log \upsilon_{act})$ is also linear for these glass formers, however, its slope slightly differs from 2, i.e., it approximately equals 1.60 and 1.70 for BMPC and GLB, respectively. However, as an opposite example, one can observe a deviation of the dependence $\log(\sqrt{\Delta C_p} dT/dp)$ from its linear approximation for PVAc at high pressures, which results in a deviation of the dependence $\log \chi_4^{max}(\log \upsilon_{act})$ from its linear approximation. Since the middle term of the right side of Eq. (5b) is a linear function of the logarithm of the activation volume only for some materials, one can claim that the dependence $\log \chi_4^{max}(\log \upsilon_{act})$ is in general nonlinear.

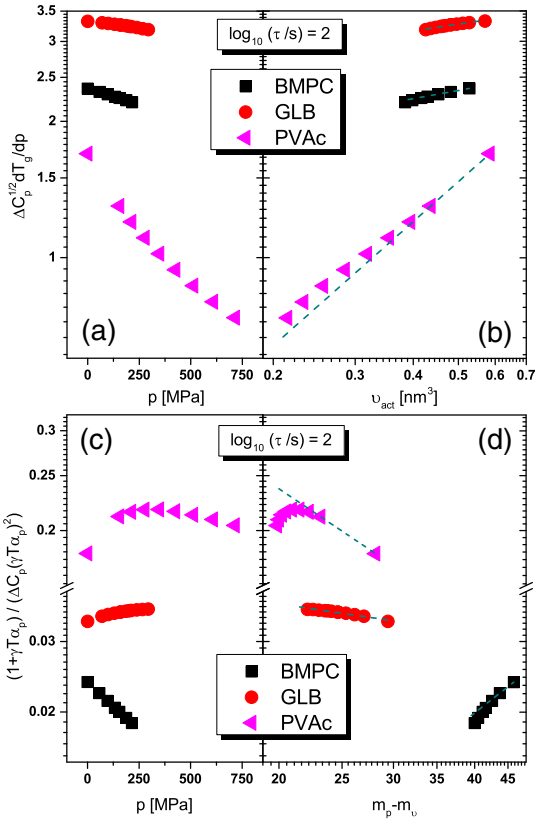

Fig. 5. Plots of the changes in the values of the middle terms of Eqs. (5b) and (6b) with varying pressure for two van der Waals liquids (BMPC and GLB) and a polymer melt (PVAc) in isochronal conditions ($\tau = 100$ s). The pressure and activation volume functions of the middle term of Eq. (5b) are represented in panels (a) and (b), respectively, whereas the plots of the middle term of Eq. (6b) vs. pressure and the difference between isobaric and isochoric fragilities are shown in panels (c) and (d), respectively. The dashed lines are used to represent the deviations of the examined dependences from the linear relationships and only in the case of the plots for BMPC and GLB in panel (b) as well as for GLB in panel (d) can be treated as successful linear approximations.

To study the correlation between the degree of the dynamic heterogeneity and the difference between isobaric and isochoric fragilities we start from Eq. (1), which estimates χ_4^{max}. Eq. (1) can be simply represented as follows $\chi_4^{max} = \frac{R\beta^2}{\Delta C_p e^2} ln^2(10) m_p^2$, and then multiplied and divided by $(m_p - m_\upsilon)^2$. Since the isobaric fragility at a constant relaxation time in the density scaling regime can be expressed by the isochoric fragility [77–79], $m_p = m_\upsilon(1 + \gamma T \alpha_p)$ (where γ is the scaling exponent that is a material constant, which can be evaluated (see Table 2) using the temperature–volume version of the entropic Avramov model [57]), the quotient of isobaric and isochoric fragilities, $m_p/m_\upsilon = 1 + \gamma T \alpha_p$, and the difference between isobaric and isochoric fragilities, $m_p - m_\upsilon = m_\upsilon \gamma T \alpha_p$. Exploiting the above relations, we can transform Eq. (1) to the following equation:

$$\chi_4^{max} = \frac{R\beta^2 ln^2(10)}{e^2} \frac{\left(1 + \gamma T \alpha_p\right)^2}{\Delta C_p \left(\gamma T \alpha_p\right)^2} \left(m_p - m_\upsilon\right)^2, \tag{6a}$$

and after taking its logarithm, we arrive at the sought after formula:

$$\log\left(\chi_4^{max}\right) = 2 \log\left(m_p - m_\upsilon\right) + \log\left(\frac{\left(1 + \gamma T \alpha_p\right)^2}{\Delta C_p \left(\gamma T \alpha_p\right)^2}\right) + \log\left(\frac{R\beta^2 ln^2(10)}{e^2}\right). \tag{6b}$$

Similarly to Eq. (5b) the last term of the right side of Eq. (6b) is constant at a constant relaxation time, thus the Eq. (6b) represents a linear

dependence of the logarithm of the degree of the dynamic heterogeneity on the logarithm of the difference between isobaric and isochoric fragilities only if the middle term of the right side of Eq. (6b) is constant, and thus a general linear dependence log χ_4^{max}(log $(m_p - m_\upsilon)$) for all materials should exist. However, as we demonstrated in Fig. 4, any general linear dependence is not observed for examined materials, which means that the middle term of the Eq. (6b) is not constant in explored pressure ranges (see Fig. 5c). Similarly to the dependence of the dynamic heterogeneity on the activation volume, log χ_4^{max} can be a linear function of log $(m_p - m_\upsilon)$ for each material separately, only if the middle term of Eq. (6b), log $\left(\frac{(1+\gamma T\alpha_p)}{\Delta C_p(\gamma T\alpha_p)^2}\right)$, is also a linear function of log $(m_p - m_\upsilon)$ to a good approximation. However, one can see deviations of log $\left(\frac{(1+\gamma T\alpha_p)}{\Delta C_p(\gamma T\alpha_p)^2}\right)$ from linear dependences on log $(m_p - m_\upsilon)$ to different extents, depending on tested materials. The linear dependence, which is represented for each tested materials by a dashed line in Fig. 5d, can be accepted to a good approximation for GLB, but it is violated for BMPC

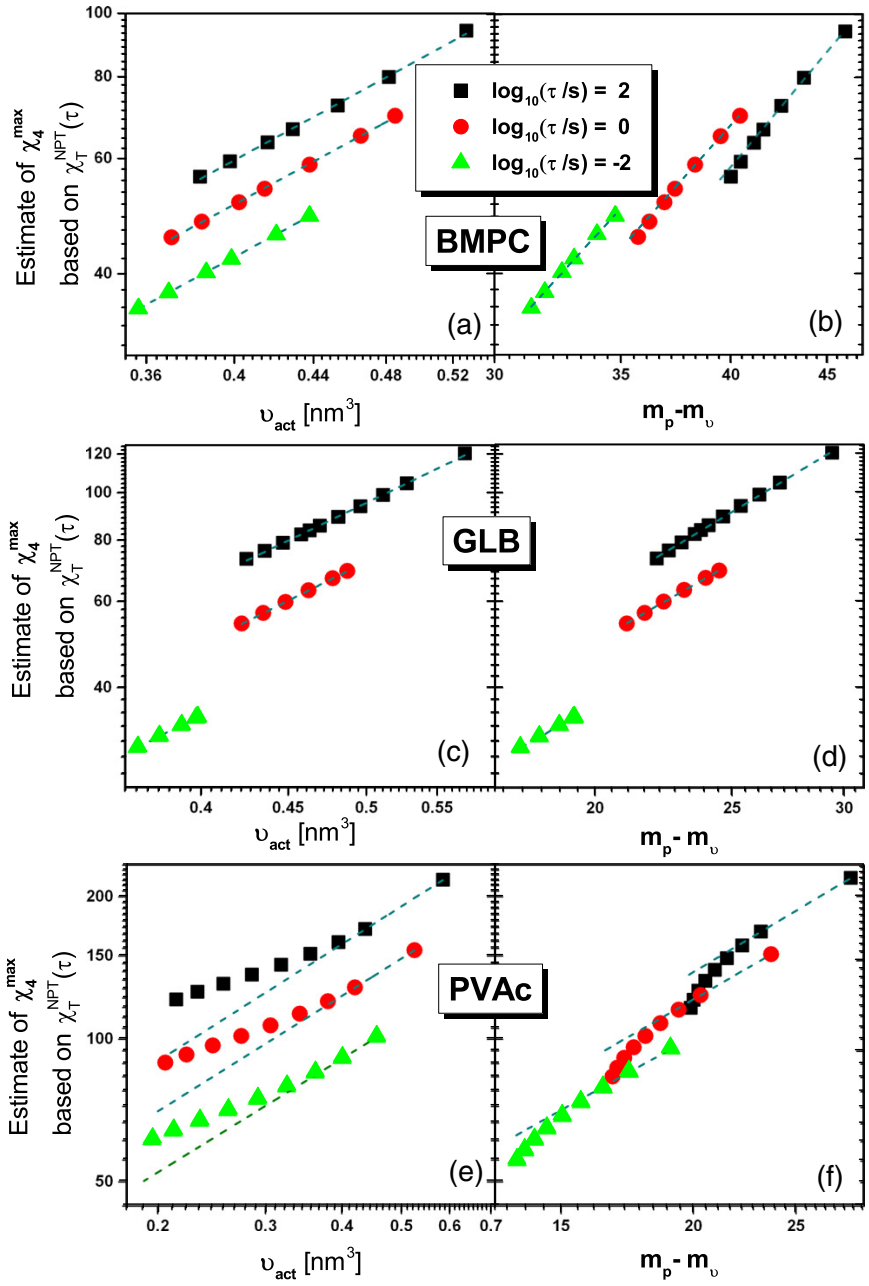

Fig. 6. Plots of the dependences of the degree of the dynamic heterogeneity on the activation volume (left panels (a), (c), and (e) for BMPC, GLB, and PVAc, respectively) and the difference between isobaric and isochoric fragilities (right panels (b), (d), and (f) for BMPC, GLB, and PVAc, respectively) along three different isochrones characterized by $\tau = 100$ s, 1 s, and 0.01 s. The dashed lines are used to represent the deviations of the examined dependences from the linear relationships and only in the case of all isochrones depicted in panels (a), (c), (d), and the isochrone at $\tau = 0.01$ s in panel (b) can be treated as successful linear approximations.

at high pressures. Interestingly, the middle term of the right side of Eq. (6b) in general non-linearly and non-monotonically depends on both pressure and the difference between isobaric and isochoric fragilities for PVAc. It causes that the examined dependence of log $\chi_4^{\max}$ on log $(m_p - m_v)$ reveals the highest degree of its curvature for PVAc among all studied materials.

The above theoretical explanations clearly show that for a given glass former we cannot in general expect any linear correlation between the dynamic heterogeneity and the activation volume as well as the dynamic heterogeneity and the difference between isobaric and isochoric fragilities in the limit of the approximation of the degree of the dynamic heterogeneity in terms of Eq. (1).

3.4. Test of the isochronal dependences log χ_4^{max}(log v_{act}) and log χ_4^{max}(log $(m_p - m_v)$) at different constant relaxation times

We have shown that any general correlations between the dynamic heterogeneity and the activation volume as well as between the dynamic heterogeneity and the difference between isobaric and isochoric fragilities are not observed for tested materials at $\tau = 100$ s. Although the above theoretical explanations are valid at each dynamic state, which is characterized by a constant relaxation time, we show here that these examined relationships behave similarly at other relaxation times, which are equal to 1 s and 0.01 s for the same three materials chosen as examples. The results for BMPC, GLB, and PVAc are presented in the double logarithmic scale in Fig. 6, where $\chi_4^{max}(v_{act})$ and $\chi_4^{max}(m_p - m_v)$ are shown in left and right panels, respectively, and the dashed straight lines are used to represent the deviations of the experimental dependences from the linear dependences. We find that the decrease in the relaxation time improves in some cases the linear approximations of the examined correlations, however, those linear approximations are fully satisfactory only in case of GLB and BMPC, where the dependence log χ_4^{max}(log $(m_p - m_v)$) of the latter material is characterized by a completely successful linear fit only along the isochrone at $\tau = 0.01$ s. It should be noted that the evident deviations of both the tested dependences from their linear approximations limited to low pressures are observed along each tested isochrone of PVAc. Thus, the degree of the dynamic heterogeneity for a given material can be in general expressed by non-linear functions of the logarithm of the activation volume and the logarithm of the difference between isobaric and isochoric fragilities under any isochronal conditions. Moreover, if these isochronal dependences can be satisfactorily approximated for a given material by linear functions at different constant structural relaxation times, the slopes of the linear dependences slightly vary, e.g., from 1.70 to 1.75 in case of log $\chi_4^{\max}$(log v_{act}) and from 1.74 to 1.60 in case of log χ_4^{max}(log$(m_p - m_v)$) for GLB between $\tau = 100$ s and $\tau = 0.01$ s.

4. Summary and conclusions

In this paper, we examine the relationships between the degree of the dynamic heterogeneity and the activation volume as well as between the degree of the dynamic heterogeneity and the difference between isobaric and isochoric fragilities. Although some linear correlations of the logarithm of the dynamic heterogeneity length scale on log v_{act} and log$(m_p - m_v)$ have been earlier suggested, we do not observe such general linear correlations at ambient and elevated pressures. Thus, we postulate that the existence of those earlier suggested linear correlations for various materials at ambient pressure results from mutual relations between values of χ_4^{max}, v_{act}, and $m_p - m_v$, for some materials, which can only exceptionally collapse onto one master straight line. In general, our study suggests that the tested linear correlations involving data for all examined materials cannot be confirmed at any constant pressure.

The main goal of our investigations reported herein was to verify whether the isochronal dependences log $\chi_4^{\max}$(log v_{act}) and log χ_4^{max}(log$(m_p - m_v)$) can be described for a given material by some linear functions to a good approximation, which has been also suggested earlier from preliminary analyses of the dynamic heterogeneity length scale under high pressure. We have established that the examined dependences in the wide pressure ranges cannot be fitted to linear functions to any sufficiently good approximation for all materials separately. It means that the cases that satisfy the linear correlations do not constitute any general rule. Therefore, we can claim that there are no general linear correlations between the dynamic heterogeneity and the activation volume as well as between the dynamic heterogeneity and the difference between isobaric and isochoric fragilities for all examined materials. In the limit of the estimate given by Eq. (1), which has been proposed for the degree of the dynamic heterogeneity by Berthier et al. [15], we explain why the linear correlations of studied dependences have not been confirmed. It should be stressed that any direct experimental determination of the dynamic heterogeneity quantified by the four-point dynamic correlation function $\chi_4(t)$ requires measuring the nonlinear response of examined samples, which is not possible to detect in the standard spectroscopy methods. However, some experiments, which can provide useful information about the dynamic heterogeneity at elevated pressure are under construction, thus the final verdict of the existence of the examined correlations should be returned in the near future.

Acknowledgment

The authors are grateful for the research project within the program MAESTRO 2, financed by the Polish National Science Center based on Decision No. DEC-2012/04/A/ST3/00337.

References

[1] G. Adam, J.H. Gibbs, J. Chem. Phys. 43 (1965) 139.
[2] L. Hong, P.D. Gujrati, V.N. Novikov, A.P. Sokolov, J. Chem. Phys. 131 (2009) 194511.
[3] L. Hong, V.N. Novikov, A.P. Sokolov, Phys. Rev. E. 83 (2011) 061508.
[4] L. Hong, V.N. Novikov, A.P. Sokolov, J. Non-Cryst. Solids 357 (2011) 351.
[5] E. Donth, The Glass Transition, Springer, Berlin, 2001.
[6] T.R. Kirkpatrick, D. Thirumalai, P.G. Wolynes, Phys. Rev. A 40 (1989) 1045.
[7] P. Viot, G. Tarjus, D. Kivelson, J. Chem. Phys. 112 (10) (2000) 368.
[8] J.P. Garrahan, D. Chandler, Phys. Rev. Lett. 89 (2002) 035704.
[9] M.D. Ediger, Annu. Rev. Phys. Chem. 51 (2000) 99.
[10] C. Bennemann, C. Donati, J. Baschnage, S.C. Glotzer, Nature (London) 399 (1999) 246.
[11] E.V. Russell, N.E. Israeloff, Nature (London) 408 (2000) 695.
[12] S. Capaccioli, G. Ruocco, F. Zamponi, J. Phys. Chem. B 112 (2008) 10652.
[13] M. Merolle, J.P. Garrahan, D. Chandler, Proc. Natl. Acad. Sci. U. S. A. 102 (10) (2005) 837.
[14] C. Toninelli, M. Wyart, L. Berthier, G. Biroli, J.-P. Bouchaud, Phys. Rev. E. 71 (2005) 041505.
[15] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, M. Pierno, Science 310 (2005) 1797.
[16] G. Biroli, J.P. Bouchaud, K. Miyazaki, D.R. Reichman, Phys. Rev. Lett. 97 (2006) 195701.
[17] A.S. Keys, A.R. Abate, S.C. Glotzer, D.J. Durian, Nat. Phys. 3 (2007) 260.
[18] R.S.L. Stein, H.C. Andersen, Phys. Rev. Lett. 101 (2008) 267802.
[19] S. Karmakar, C. Dasgupta, S. Sastry, Proc. Natl. Acad. Sci. U. S. A. 106 (2009) 3675.
[20] R. Candelier, O. Dauchot, G. Biroli, Phys. Rev. Lett. 102 (2009) 088001.
[21] G. Williams, J. Non-Cryst. Solids 131 (1991) 1.
[22] K.L.J. Ngai, Non-Cryst. Solids 275 (2000) 7.
[23] K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, A.P. Sokolov, M. Paluch, Phys. Rev. Lett. 111 (2013) 125701.
[24] A. Grzybowski, K. Kołodziejczyk, K. Koperwas, K. Grzybowska, M. Paluch, Phys. Rev. B 85 (2012) 220201 (R).
[25] A. Grzybowski, K. Koperwas, K. Kolodziejczyk, K. Grzybowska, M. Paluch, J. Phys. Chem. Lett. 4 (2013) 4273.
[26] D. Fragiadakis, R. Casalini, C.M. Roland, Phys. Rev. E. 84 (2011) 042501.
[27] K.L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, C.M. Roland, J. Phys. Chem. B 109 (17) (2005) 356.
[28] W. Schirmacher, B. Schmid, C. Tomaras, G. Viliani, G. Baldi, G. Ruocco, T. Scopigno, Phys. Status Solidi C 5 (2008) 862.
[29] E. Duval, A. Boukenter, T. Achibat, J. Phys. Condens. Matter 2 (1990) 10227.
[30] A.P. Sokolov, A. Kisliuk, M. Soltwisch, D. Quitmann, Phys. Rev. Lett. 69 (1992) 1540.
[31] S.R. Elliott, Europhys. Lett. 19 (1992) 201.
[32] A.P. Sokolov, R. Calemczuk, B. Salce, A. Kisliuk, D. Quitmann, E. Duval, Phys. Rev. Lett. 78 (1997) 2405.
[33] S. Whitelam, L. Berthier, J.P. Garrahan, Phys. Rev. Lett. 92 (2004) 185705.

[34] G. Biroli, J.P. Bouchaud, Europhys. Lett. 67 (2004) 21.
[35] M.M. Hurley, P. Harrowell, Phys. Rev. E. 52 (1995) 1694.
[36] L. Berthier, Physics 4 (2011) 42.
[37] C. Donati, S. Franz, S.C. Glotzer, G. Parisi, J. Non-Cryst. Solids 307–310 (2002) 215.
[38] L. Berthier, Phys. Rev. E. 69 (2004) 020201.
[39] C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hoˆte, G. Tarjus, Phys. Rev. E. 76 (2007) 041510.
[40] L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, D.R. Reichman, J. Chem. Phys. 126 (2007) 184503.
[41] L. Berthier, G. Biroli, J.-P. Bouchaud, W. Kob, K. Miyazaki, D.R. Reichman, J. Chem. Phys. 126 (2007) 184504.
[42] A.R. Abate, D.J. Durian, Phys. Rev. E. 76 (2007) 021306.
[43] Rotman, E. Eisenberg, Phys. Rev. Lett. 105 (2010) 225503.
[44] A. Grzybowski, M. Paluch, K. Grzybowska, S. Haracz, J. Chem. Phys. 133 (2010) 161101.
[45] L. Comez, S. Corezzi, D. Fiorento, Phil. Mag. 84 (2004) 1521.
[46] W. Heinrich, B. Stoll, Progr. Colloid Polym. Sci. 78 (1988) 37.
[47] A. Grzybowski, K. Grzybowska, M. Paluch, A. Swiety, K. Koperwas, Phys. Rev. E. 83 (2011) 041505.
[48] A. Grzybowski, M. Paluch, K. Grzybowska, J. Phys. Chem. B 113 (2009) 7419.
[49] A. Grzybowski, S. Haracz, M. Paluch, K. Grzybowska, J. Phys. Chem. B 114 (2010) 11544.
[50] A. Grzybowski, M. Paluch, K. Grzybowska, Phys. Rev. E. 82 (2010) 013501.
[51] A. Grzybowski, K. Koperwas, M. Paluch, Phys. Rev. E. 86 (2012) 031501.
[52] A. Grzybowski, K. Koperwas, M. Paluch, J. Chem. Phys. 140 (2014) 044502.
[53] K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, J. Pionteck, A.P. Sokolov, M. Paluch, Phys. Rev. E. 86 (2012) 041502.
[54] E. Masiewicz, A. Grzybowski, A.P. Sokolov, M. Paluch, J. Phys. Chem. Lett. 3 (2012) 2643.
[55] A. Grzybowski, K. Koperwas, A. Swiety-Pospiech, K. Grzybowska, M. Paluch, Phys. Rev. B 87 (2013) 054105.
[56] M. Chorążewski, A. Grzybowski, M. Paluch, Phys. Chem. Chem. Phys. (2014), http://dx.doi.org/10.1039/C4CP02350A.
[57] R. Casalini, U. Mohanty, C.M. Roland, J. Chem. Phys. 125 (2006) 014505.
[58] I. Avramov, J. Non-Cryst. Solids 262 (2000) 258.
[59] S. Hensel-Bielowka, J. Ziolo, M. Paluch, C.M. Roland, J. Chem. Phys. 117 (2002) 2317.
[60] Z. Wojnarowska, K. Adrjanowicz, K. Kaminski, L. Hawelek, M. Paluch, J. Phys. Chem. B 114 (14) (2010) 815.
[61] M. Naoki, H. Endou, K. Matsumoto, J. Phys. Chem. 91 (1987) 4169.
[62] M. Paluch, C.M. Roland, A. Best, J. Chem. Phys. 117 (2002) 1188.
[63] C.M. Roland, R. Casalini, Macromolecules 36 (2003) 1361.
[64] Z. Wojnarowska, M. Paluch, A. Grzybowski, K. Adrjanowicz, K. Grzybowska, K. Kaminski, P. Wlodarczyk, J. Pionteck, J. Chem. Phys. 131 (2009) 104505.
[65] S. Hansel-Bielowka, J.R. Sangoro, Z. Wojnarowska, L. Hawelek, M. Paluch, Phys. Chem. Chem. Phys. 15 (2013) 9300.
[66] K. Adrjanowicz, K. Kaminski, Z. Wojnarowska, M. Dulski, L. Hawelek, S. Pawlus, M. Paluch, J. Phys. Chem. B 114 (2010) 6579.
[67] Z. Wojnarowska, Y. Wang, J. Pionteck, K. Grzybowska, A.P. Sokolov, M. Paluch, Phys. Rev. Lett. 111 (2013) 225703.
[68] Z. Wojnarowska, K. Adrjanowicz, P. Wlodarczyk, E. Kaminska, K. Kaminski, K. Grzybowska, R. Wrzalik, M. Paluch, K.L. Ngai, J. Phys. Chem. B 113 (2009) 12536.
[69] R. Casalini, C.M. Roland, J. Chem. Phys. 119 (2003) 11951.
[70] K. Grzybowska, S. Pawlus, M. Mierzwa, M. Paluch, K.L. Ngai, J. Chem. Phys. 125 (2006) 144507.
[71] M. Paluch, J. Gapinski, A. Patkowski, E.W. Fischer, J. Chem. Phys. 114 (2001) 8048.
[72] C. Alba-Simionesco, C. Dalle-Ferrier, G. Tarjus, Am. Inst. Phys. Conf. Proc. 1518 (2013) 527.
[73] L. Bøhling, T.S. Ingebrigtsen, A. Grzybowski, M. Paluch, J.C. Dyre, T.B. Schrøder, New J. Phys. 14 (2012) 113035.
[74] A. Grzybowski, K. Grzybowska, J. Zioło, M. Paluch, Phys. Rev. E. 74 (2006) 041503.
[75] A. Grzybowski, K. Grzybowska, J. Zioło, M. Paluch, Phys. Rev. E. 76 (2007) 013502.
[76] K. Grzybowska, M. Paluch, A. Grzybowski, S. Pawlus, S. Ancherbak, D. Prevosto, S. Capaccioli, J. Phys. Chem. Lett. 1 (2010) 1170.
[77] R. Casalini, C.M. Roland, Phys. Rev. B 71 (2005) 014210.
[78] C. Alba-Simionesco, G. Tarjus, J. Non-Cryst. Solids 352 (2006) 4888.
[79] K. Mpoukouvalas, G. Floudas, G. Williams, Macromolecules 42 (2009) 4690.

4.4. TERMODYNAMICZNE KONSEKWENCJE KINETYCZNEJ NATURY PRZEJŚCIA SZKLISTEGO

Autorzy:

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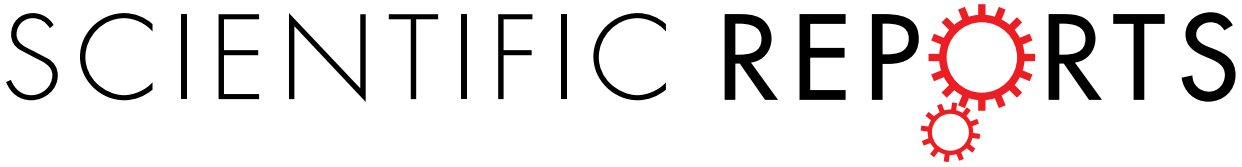
Referencja: Sci. Rep. 5, 17782 (2015)

Skrót:

W artykule rozważamy przejście szkliste jako proces kinetyczny i wprowadzamy jedno uniwersalne równanie na ciśnieniowy współczynnik temperatury przejścia szklistego dT_g / dp, który jest termodynamiczną charakterystyką tego procesu. Nasze wnioski podważają powszechne oczekiwania dotyczące kluczowych cech procesu transformacji cieczy przechłodzonej w szkło, ponieważ sugerują, że bez wykorzystania dodatkowego warunku spełnionego w przejściu szklistym, wyprowadzenie dwóch niezależnych równań na dT_g / dp jest niemożliwe. Zatem, niewykonalne jest otrzymanie jakiejkolwiek relacji pomiędzy współczynnikami termodynamicznymi, która byłaby odpowiednikiem znanej relacji Prigogine'a-Defaya dla przejścia szklistego. Ponadto poprzez porównanie przewidywań naszego równania na dT_g / dp i wzorów Ehrenfesta, znajdujemy wyżej wspomniane dodatkowe ograniczenie, które musi być spełnione aby stosować relację Prigogine-Defaya w przejściu szklistym.



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Thermodynamic consequences of the kinetic nature of the glass transition

Received: 28 August 2015
Accepted: 03 November 2015
Published: xx xx xxxx

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In this paper, we consider the glass transition as a kinetic process and establish one universal equation for the pressure coefficient of the glass transition temperature, dT_g/dp, which is a thermodynamic characteristic of this process. Our findings challenge the common previous expectations concerning key characteristics of the transformation from the liquid to the glassy state, because it suggests that without employing an additional condition, met in the glass transition, derivation of the two independent equations for dT_g/dp is not possible. Hence, the relation among the thermodynamic coefficients, which could be equivalent to the well-known Prigogine-Defay ratio for the process under consideration, cannot be obtained. Besides, by comparing the predictions of our universal equation for dT_g/dp and Ehrenfest equations, we find the aforementioned supplementary restriction, which must be met to use the Prigogine-Defay ratio for the glass transition.

The fundamental mechanism underlying the glass transition phenomena in non-crystallizing liquids is perhaps the most challenging problems in condensed matter physics and active areas of research since 1950. In the quest to deliver a complete explanation of the transformation from metastable supercooled state to the non-equilibrium glassy state, abundant theoretical and experimental studies have been devoted. Particularly, the change in glass transition temperature (T_g) as a function of pressure and its connection with the thermodynamic coefficients, which provides a suitable parameter to elucidate the nature of glass transition, has been intensively examined. Numerous experimental studies on different glass-formers reveal that the pressure coefficient of the glass transition temperature is substantial in the case van der Waals liquids (*i.e.*, $dT_g/dp \approx 0.25$ K/MPa)[1,2], whereas for hydrogen-bonded liquids the change of T_g weakly depends on pressure (*i.e.*, $dT_g/dp \approx 0.1$ K/MPa)[3,4]. Certainly, the development of a suitable universal relation between dT_g/dp and the key thermodynamic coefficients (*i.e.*, isobaric expansivity (α_p), isothermal compressibility (κ_T), isobaric (C_p) and isochoric (C_v) specific heats) has become a fundamental problem of the theoretical investigation of glass physics.

In the past, many efforts have been gained in the past to explain the nature of the glass transition. It is well established, that at the glass transition, Gibbs free energy and its first derivatives (*i.e.*, volume v and entropy S) are continuous, while second derivatives are connected to thermodynamic coefficients and show step-like behavior in the vicinity of T_g. Eventually, attempts have been made to consider the liquid-glass transition as a second-order phase transition. Some efforts were undertaken to verify both Ehrenfest equations (eqs. (1) and (2)) and the Prigogine-Defay ratio (eq. (3))[5–7].

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$$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\Delta\alpha_p} \tag{1}$$

$$\frac{dT}{dp} = vT_g\frac{\Delta\alpha_p}{\Delta C_p}, \text{ and} \tag{2}$$

$$\Pi = \frac{1}{vT_g}\frac{\Delta C_p\Delta\kappa_T}{\left(\Delta\alpha_p\right)^2} \equiv 1, \tag{3}$$

where Δ denotes the differences between respective coefficients in the liquid and the glassy states. However, it is worth noting that in the case of a second-order phase transition the system goes from one equilibrium state to the other, whereas at the glass transition, the system is transferred from the (metastable) equilibrium into the non-equilibrium state, which is the glass. Therefore, it is not surprising that the majority of experimental investigations of "Π" revealed that its value differs from unity[5,8–10]. Another approach to describe the liquid-glass transition, which is certainly worthy of attention, is the concept of order parameters, which was introduced by Donder and van Rysselberghe[11]. It suggests that the state of the system in both the equilibrium and non-equilibrium states depends on the thermodynamic intensive parameters (temperature, pressure) and a number of order parameters. Then, Simon proposed that the glass transition could be considered as a process at which the system becomes suddenly kinetically frozen in[12], *i.e.*, the structural reorganization cannot follow anymore the change of temperature and/or pressure. Assuming that only one order parameter is sufficient to describe the structural differences between the liquid and the glass, both Ehrenfest equations and hence value $\Pi = 1$ were theoretically obtained by Davies and Jones [5,10,13,14]. In this context, it has to be noted that equation (1), which is usually not fulfilled[14–18], incorporates κ_T also measured in the nonequilibrium glassy state, which makes it difficult to verify experimentally[19]. On the other hand, equation (2) seems to hold reasonably well for many systems, although not for all[20,21]. Nevertheless, the Prigogine-Defay ratio is seen as an indicator of the complexity; the number suggesting the degree to which the liquid fails to be described by a single order parameter[22]. However, treating vitrification in terms of Simon's models[12], one assumes that the order parameter is defined independently on the rate of external parameters changes as a function of temperature and pressure, which in general is not true, because for dense systems during the cooling to T_g and below the order parameter cannot follow the changes of the external parameters (*e.g.*, temperature) and deviates from its equilibrium value[23]. This behavior occurs when the time scale of changes of the external parameter become comparable with the characteristic relaxation time of the system τ_R *e.g.*, the structural relaxation time τ_α. Therefore, the transformation from the liquid to the glassy state is expected to have a kinetic, rather than thermodynamic, origin. It is consistent with the one of the most important conclusions from the long history of the research on the glass transition process, i.e., the dependence of T_g on the experiment (cooling or heating) rate. Hence, many efforts have been made to formulate the definition of the glass transition by considering it as a purely kinetic process. First attempts were made by Bartenev[24] and Jones[25], in 1949. Two years later, from a general examination of the cooling process[24,26], Bartenev derived the relation $\left|\frac{dT}{dt}\tau_R\right|_{T_g} = const.$[24], which was experimentally corroborated for different materials[27,28]. It is worth noting that an identical formula can be obtained from the chemical reaction model when one employs certain additional conditions, which are commonly met in the glass transition, as Volkenstein and Ptizyn presented[24]. They also noticed that the constant term occurs in the Bartenev's relation should weakly depend on T_g. Nevertheless, later and detailed examinations performed by Moynihan *et al.*[29] have confirmed that the aforementioned relationship is perfectly satisfied, and then it has become regarded as generally binding at the glass transition[30,31]. Thereby, the general understanding has been shaped, according to which, only the value of $\tau_R|_{T_g} \equiv \tau_g$ defines the glass transition, if the constant cooling rate is applied to different isobaric states. In this context, the interesting considerations given by Hodge[32], to the Deborah number, which is defined as the ratio of timescales of the observed and the observer, $d\tau/dt$, are worthy of mentioning. According to them the glass transition is seen when the above two timescales cross over and then Deborah number passes through unity. Then in the temperature domain, that is explored most thoroughly, a Deborah number of unity that defines an average T_g can be expressed in terms of the rate of change of some characteristic timescale τ, determined during cooling: $\frac{d\tau}{dt} = \frac{d\tau}{dT}\frac{dT}{dt} \approx 1$. Since the temperature dependence of relaxation time for many processes is given by the empirical Vogel-Tamman-Fulcher equation, at the isobaric conditions the above criterion results in the following relation $\tau_g\frac{dT}{dt} \approx T_g/(m_p \ln 10)$, where $m_p = \left(\frac{\partial \log \tau}{\partial T/T_g}\right)_p\Big|_{T=T_g}$ is the isobaric fragility. Assuming that the glass transition is approached at a constant cooling rate, τ_g becomes

proportional to T_g/m_p. Then, combining it with Bartenev relation, one obtains that the constant value depends on T_g/m_p, which implies that values of τ_g do not have to be invariant for all isobaric conditions. However, T_g/m_pestablished by experimental data of the structural relaxation times τ_α, obtained from dielectric spectroscopy of different glass formers, is a slowly varying function of the pressure, which usually results in the increase in $\tau_\alpha|_{T_g}$ in only a few seconds with increasing the pressure from 0 to 200 to 300 MPa[33]. Hence, the glass transition can be defined, with very good agreement, by a constant value of $\tau_\alpha|_{T_g}$ (which for simplicity in the later part of the letter will be denoted by τ_g). Following the general wisdom, in this paper we examine the glass transition as a kinetic process and consequently on this basis, we derive one universal equation for the pressure coefficient of the glass transition temperature. We show that by considering the dependence of the characteristic relaxation of the system, defined by the structural relaxation time τ_α, on different external parameters, one can obtain equations for dT_g/dp, which originates from one universal equation. In this context, they are not independent, and hence the relation equivalent to the Prigogine-Defay ratio cannot be established for the glass transition, at least without employment of an additional condition met in this process. The three above possible equations for dT_g/dp, obtained in the cases of dependences, $\tau_\alpha(T, v)$, $\tau_\alpha(T, p)$, and $\tau_\alpha(T, S)$, have been verified. We also show that predictions based on the above equations are consistent within a wide range of pressures. Moreover, we analyze our universal equations in terms of the Simon's model[12] and we find for which systems the structural differences between the liquid and the glass can be described by only one order parameter.

Results

The structural relaxation time τ_α depends on many thermodynamic quantities, *e.g.*, temperature, pressure, volume, and entropy. However, only two of them can be changed independently from the others. Since temperature is the physical quantity most often controlled in different experiments, we propose that in the most convenient way, the structural relaxation time can be considered as a function of T and another thermodynamic quantity X. Then, the complete differential of the structural relaxation time $d\tau_\alpha(T, X)$, at the glass transition defined at a constant value of τ_g, equals $0 = d\tau_g(T, X) = \left(\frac{\partial\tau}{\partial T}\right)_X dT + \left(\frac{\partial\tau}{\partial X}\right)_T dX$. On the other hand, X is a function of two independent thermodynamic quantities that can be selected from many of the other thermodynamic quantities. One of the most natural selections is T and p, and then $\left(\frac{\partial p}{\partial T}\right)_X \left(\frac{\partial X}{\partial p}\right)_T \left(\frac{\partial T}{\partial X}\right)_p = -1$. Using the above relation between thermodynamic quantities we can rewrite the complete derivative of τ_g and then $0 = -\left(\frac{\partial\tau}{\partial p}\right)_X \left(\frac{\partial X}{\partial T}\right)_p dT + \left(\frac{\partial\tau}{\partial p}\right)_T dX$. Since, $\left(\frac{\partial\tau}{\partial p}\right)_X = -\left(\frac{\partial\tau}{\partial X}\right)_p \left(\frac{\partial X}{\partial p}\right)_\tau$, the latter equation transforms to $0 = \left(\frac{\partial\tau}{\partial T}\right)_p \left(\frac{\partial X}{\partial p}\right)_\tau dT + \left(\frac{\partial\tau}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T dX$, where expressions for the isobaric and the isothermal fragility ($m_T = (\partial \log \tau/\partial(v_g/v))_T|_{v=v_g}$) can be exploited. As we have mentioned above, X is a function of T and p, thus the formula for its complete derivative is expressed as follows $dX = \left(\frac{\partial X}{\partial T}\right)_p dT + \left(\frac{\partial X}{\partial p}\right)_T dp$. Using it, we obtain the required equation for the pressure coefficient of the glass transition temperature, which takes the subsequent form $\frac{dT_g}{dp} = \frac{\kappa_T\left(\frac{\partial X}{\partial v}\right)_T}{\frac{-m_p}{m_T\kappa_T v T}\left(\frac{\partial X}{\partial p}\right)_\tau + \alpha_p\left(\frac{\partial X}{\partial v}\right)_p}$. The term, which appears in the denominator and consists of quotient of the isobaric and the isothermal fragility, can be transformed to $\frac{m_v}{m_T T}\left(\frac{\partial X}{\partial v}\right)_\tau$, where $m_v = (\partial \log \tau/\partial(T_g/T))_v|_{T=T_g}$ is the isochoric fragility. In conclusion, the general equation for the pressure coefficient of the glass transition temperature takes the following form

$$\frac{dT_g}{dp} = \frac{\kappa_T\left(\frac{\partial X}{\partial v}\right)_T}{\frac{m_v}{m_T T}\left(\frac{\partial X}{\partial v}\right)_\tau + \alpha_p\left(\frac{\partial X}{\partial v}\right)_p}, \tag{4}$$

where m_v/m_T reflects the relative roles of T and v in the molecular dynamics, whereas X is any thermodynamic quantity, *e.g.*, v, p or S. Thus, one can easily obtain several expressions for dT_g/dp, *e.g.*,

$$\frac{dT_g}{dp} = \frac{\kappa_T}{\frac{m_v}{m_T T} + \alpha_p}, \tag{5}$$

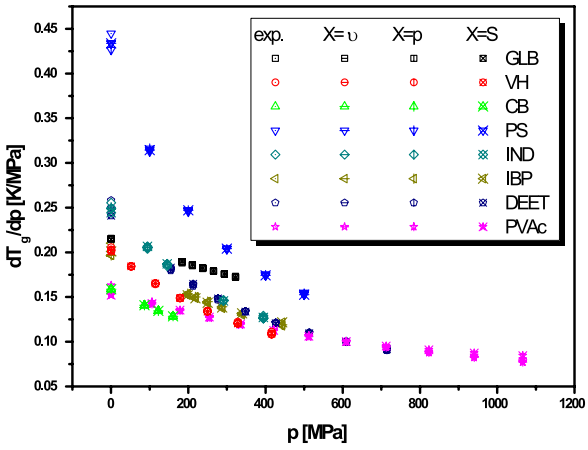


Figure 1. Values of the pressure coefficient of the glass transition temperature calculated from equations (5–7), $X = v$, p, S respectively, and obtained from analysis of experimental measurements (exp.) for glibenclamide (GLB), verapamil hydrochlorine (VH), carvedilol base (CB), polystyrene (PS) (all in Ref. 33), indometacin (IND)[59], ibuprofen (IBP)[60], N, N-dimethyl-3-methylbenzamide (DEET), and polyvinylacetate (PVAc). The glass transition for CB is defined by $\log(\tau_\alpha/s) = 1.625$, whereas for DEET and PVAc by $\log(\tau_\alpha/s) = 2$.

$$\frac{dT_g}{dp} = \frac{m_T \kappa_T T}{m_p}, \tag{6}$$

$$\frac{dT_g}{dp} = \frac{\alpha_p}{\frac{m_v}{m_T T}\left(\frac{\partial S}{\partial v}\right)_\tau + \frac{C_p}{vT}}, \tag{7}$$

if one substitutes X for volume (eq. (5)), pressure (eq. (6)), entropy (eq. (7)) or another physical quantity. The predictions of above equations for dT_g/dp and values of this coefficient obtained from analysis of the experimental measurements are presented in Fig. 1, which shows that the values of dT_g/dp calculated from equations (5), (6), and (7) are very consistent with each other over a wide range of pressures and as well as to that received from the analysis of the experimental data. In this context, it has to be noted that equation (5) was earlier successfully verified at ambient pressure for many glass-forming liquids that belong to the different material groups[33].

It is worth noting that the universal character of the equivalent equations (5)–(7) can be extended beyond the assumed case of the dependence $\tau(T, X)$. Considering the density scaling laws for τ and S (discussed later for τ and in the Supplementary Information for S), we have very recently argued[34] that the structural relaxation time can be in general a volume-entropy function $\tau(v, S)$. Then, equation (5) also remains valid as shown in Supplementary Information.

Discussion

The excellent agreement between values of dT_g/dp predicted by equations (5)–(7) is not surprise since all equations are received from equation (4). It has to be mentioned that employing the relation between fragilities $m_p = m_v + m_T T_g \alpha_p$[35]; one can easily transform equation (6) to equation (5) as well as by using the thermodynamic relation $\left(\frac{\partial S}{\partial v}\right)_\tau = \left(\frac{\partial S}{\partial v}\right)_T + \left(\frac{\partial S}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_\tau$, equation (7) can be converted to equation (5). Taking the above into account, we can expect that knowledge of the relationship between any X and v enables transformation of whichever equation for dT_g/dp resulted from equation (4) to equation (5). Besides, derivation of two independent equations for dT_g/dp, and an establishment of the relation among the thermodynamic coefficients at the glass transition (corresponding to the Prigogine-Defay ratio), is not possible, at least based on only the kinetic description of this process. So, in order to establish the relation equivalent to equation (3) that is satisfied at the glass transition, we must employ an additional condition met in this process. This has been done in Ref. 36 in which Eq. (5), which is the exceptional form of equation (5) (derived from the density scaling law, what will be discussed later), is connected with one of the Ehrenfest equations. In the next paragraph we present the derivation of the Ehrenfest equations from our universal equation for the pressure coefficient of the glass transition

temperature. However, now we can mention that this procedure requires additional assumptions and hence equation (5) from ref. 36 cannot be simply transformed to one of Ehrenfest equations. Therefore, the main equation in the mentioned paper, i.e., equation (7), results from the connection of two independent equations and is not the tautology.

In this paragraph we consider the universal equation for the pressure coefficient of the glass transition temperature in terms of the Simon's model employed by Davies and Jones[10], to give a new look at the system for which the Prigogine-Defay ratio should be valid, *i.e.*, single order parameter systems. According to simplification of the Simon's model used by Davies and Jones, the glass transition takes place at a singular T_g, at which the order parameter became kinetically frozen-it. Then, v and S of the metastable liquid (l) and the glass (g) have the same values, which implies that the configurational volume $v_C = v_l - v_g$ and entropy $S_C = S_l - S_g$ equal 0. Since, X introduced by us in equation (4), can be any thermodynamic quantity, there is nothing to preclude the consideration dependence of the characteristic relaxation time of the system on configurational values e.q. v_C or S_C. In this way, equation (4) takes following forms

$$\frac{dT_g}{dp} = \frac{\Delta\kappa_T}{\frac{m_v}{m_T}\frac{1}{T} + \Delta\alpha_p} \tag{8}$$

$$\frac{dT_g}{dp} = \frac{\Delta\alpha_p}{\frac{m_v}{m_T}\frac{1}{T}\left(\frac{S_C}{v}\right)_\tau + \frac{\Delta C_p}{vT}} \tag{9}$$

for X given by v_C and S_C respectively. Now, it can be seen that equations (8) and (9) will become identical with equations (1) and (2) if the quotient of isochoric and isothermal fragility equals 0, which implies that $m_v \to 0$ or $m_T \to \infty$. Both the restrictions reflect one possible but limited behavior of the molecular dynamics, *i.e.*, the situation at which molecular dynamics is controlled only by local density fluctuations. Thereby, the so-called "free volume model" is expected to be suitable for single order parameter liquids. Moreover, it has to be noted that the Ehrenfest equations are limiting cases of our universal equation for dT_g/dp, which seems to be much more general. On the other hand, if only fluctuations of the temperature govern the molecular dynamics, m_T and m_v behave conversely to before, and hence $dT_g/dp = 0$, which indeed reflects the situation at which the glass transition occurs at constant temperature independently of pressure and hence volume.

An additional finding, which advances our knowledge of the single order parameter systems, can be deduced from the density scaling idea. It is worth mentioned that alternative study of the so-called linear Prigogine-Defay ratio in the context of the density scaling has been very recently performed[37]. Density scaling postulates that the relaxation time of the system can be expressed by only one variable as follows, $\tau(\Gamma)$, where Γ is a function of T and v. In the most common form, which has been experimentally validated for more then 100 van der Waals liquids and polymers, $\Gamma = Tv^{\gamma}$[38–41] where γ is a scaling exponent, which is only material dependent. One of the consequences of the above form of the density scaling is a potential connection between γ and quotient of isochoric and isothermal fragility, $m_T/m_v = \gamma$ [35]. Then, equations (5) and (6) can be expressed in the following form $\frac{dT_g}{dp} = \frac{T\kappa_T}{1/\gamma + T\alpha_p}$, whereas equation (7) transforms to $\frac{dT_g}{dp} = \frac{T\alpha_p}{\frac{1}{\gamma}\left(\frac{\partial S}{\partial v}\right)_\tau + \frac{C_p}{v}}$. Both new variants of our universal equation for dT_g/dp deserve special attention because remarkably, many computer simulations of molecular dynamics confirm the connection between γ and an effective exponent used to model the repulsive part of intermolecular potential[42–47]. For dense systems, the physically relevant intermolecular potential can be successfully approximated by an effective IPL potential consisted of a dominating Inverse Power Law term for repulsive interactions (proportional to the power of intermolecular distance $r^{-3\gamma}$) and small nearly constant background reflecting attractive forces. Taking into account the previously mentioned issue of the "free volume model", systems which molecular dynamics is controlled only by the density fluctuations, may be modeled by the effective IPL potential, where the power of intermolecular distance tends to infinity, $\gamma \to \infty$. Therefore, they become similar to the hard sphere systems with small and constant background reflecting attractive forces. So, we can expect that the Prigogine-Defay ratio describes the relation among thermodynamic coefficients at the glass transition for systems modeled, *e.g.,* by the hard sphere potential. However, the formulation of the precise definition of the order parameter, which became kinetically frozen-in at the glass transition, remains an open issue in glassy physics.

At the end, we provide a comment about the excellent work of J.W.P. Schmelzer[7], in which author introduced the new general criterion for the glass transition, which consider the cooling or heating rates, $\left\{\frac{1}{T}\left|\frac{dT}{dt}\right|\tau_R\right\}\Big|_{T=T_g} \cong const.$, where τ_R is a characteristic relaxation time of the system. On the basis of the above criterion, the author derived the equation for $\frac{dT_g}{dp} = \frac{-(\partial\tau_R/\partial p)_T}{(\partial\tau_R/\partial T)_p - \tau_R/T}$ (equation (41) in ref. 7).

Later, Schmelzer examined his equation in the limiting case of the "free volume model" and the "entropy-based approach". As a result, he obtained $dT_g/dp = \kappa_T/\alpha_p$ for the "free volume systems" as well as $dT_g/dp = vT\Delta\alpha_p/\Delta C_p$, which is one of the Ehrenfest equations (eq. (2)), for the "entropy-based approach", *i.e.*, considering the relaxation times as a quantity, which depends on the temperature and the activation energy determined by the entropy. (respectively equations (46) and (50) in ref. 7) It has to be noted that our universal equation for the pressure coefficient of the glass transition temperature (eq. (4)) considered in terms of the temperature-pressure dependence of the relaxation time (eq. (5)) and the "free volume model" provides an expression for dT_g/dp, which is identical with that derived by Schmelzer for these limiting cases under consideration. However, a more intriguing fact is that Schmelzer established one of the Ehrenfest equations employing only the "entropy-based approach", because this approach to describe the molecular dynamics, is not dedicated only to the systems which dynamics is governed solely by the local volume fluctuations. This finding is in contrast to our result since in the previous paragraph we noticed that the use of "free volume model" is necessary to obtain the Ehrenfest equations from our universal equation for dT_g/dp. The only assumption made by Schmeltzer during his analysis is $\tau_R/T \ll (\partial\tau_R/\partial T)_p$, which results that τ_R/T can be neglected. It has to be mentioned that the author emphasizes that the validity of the above restriction is limited. However, we want to show that using the following thermodynamic relation $\left(\frac{\partial\tau_R}{\partial T}\right)_p = \left(\frac{\partial\tau_R}{\partial T}\right)_v + \left(\frac{\partial\tau_R}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$; one can rewrite the denominator under consideration and then $\tau_R/T \ll m_T\left(\frac{m_v}{Tm_T} + \alpha_p\right)$, which is fulfilled independently of T and α_p when $m_T \to \infty$. Thus, Schmeltzer obliviously limited his analysis to the "free volume model", and hence the "entropy based approach" employed by the author is, in fact, suitable only for the system, the dynamics of which is controlled purely by the fluctuations of volume. The presence of ΔC_p and $\Delta\alpha_p$ in the expression derived by Schmeltzer result from the entropy model used by him, *i.e.*, Adam-Gibbs model, which considers an influence of the configurational value of the entropy on the relaxation time. It is also worth noting that the term τ_R/T results from the consideration of experiment (cooling or heating) rate in Schmelzer's general criterion for the glass transition, thus its omitting, which is caused by the assumption that $\tau_R/T \ll (\partial\tau_R/\partial T)_p$, limits the predictions of the above criterion to conditions at which the glass transition is characterized by a constant value of characteristic relaxation time. In this way, the results obtained by Schmelzer are consistent in a whole with our universal equation for dT_g/dp. However, Schmelzer's work draws our attention to the consideration of cooling or heating rate as a promising opportunity to establish of another sought after condition met in the glass transition. Unfortunately, the general criterion proposed by the author seems to be not suitable for real materials, because one obtains that $\left\{\left|\frac{dT}{dt}\right|v^\gamma\right\}\Big|_{T=T_g} \cong const.$ after considering it in terms of the density scaling, $\tau_R = \Gamma(Tv^\gamma)$, and then for a constant value of γ, the glass transition should takes place at a constant volume in varying thermodynamic conditions (T and P), which is not true. Therefore, another form of the general criterion for the glass transition should be found, if it is possible.

In summary, we have derived a new general equation for the pressure coefficient of the glass transition temperature, equation (4), based on the kinetic definition of the process was experimentally verified. The ultimate advantage of our new equation is its universality, *i.e.*, it does not depend on the physical quantities, which describe the dependence of the relaxation time of the system. The consequence of the existence of one universal equation for dT_g/dp is the fact that the derivation of the two independent equations for dT_g/dp is not possible, at least without use of an additional condition, met in the glass transition. Our finding suggests that the relation equivalent to the Prigogine-Defay ratio, which results from a combination of the two independent equations for dT_g/dp, might not exist at the glass transition. For an example, we present three different equations for the pressure coefficient of the glass transition temperature, equations (5), (6), and (7), from which, anyone can be transformed to another. It should be mentioned that the above conclusion are proper for any process, which occurs at isochronal conditions, e.g., for nematic-isotropic transition[48–51] or smecticE-isotropic transition[52] observed in liquid crystals. Moreover, we show that the well-known Ehrenfest equations can be derived from our universal equation for dT_g/dp, when terms of the Simon's model are employed, as Davies and Jones did when they obtained the expressions for dT_g/dp suitable for the single order parameter systems, *i.e.*, Ehrenfest equations. Since a possibility of use of our universal equation for dT_g/dp does not depend on the number of order parameters, we deduce that the molecular dynamics of single order parameter systems must obey an additional restriction, *i.e.*, the limiting case of "free volume model" must be employed. Thereby, our study reveals an important feature of the molecular dynamics of the single order parameter systems, *i.e.*, its exclusive dependence on the local density fluctuations. It suggests that the structural differences between the liquid and the glass for the hard sphere systems can be described by only one order parameter. Thus, we believe that the further studies of a dependence of order parameter on cooling or heating rates may give an answer as to whether or not another restriction for the glass transition exists, and hence some relationship among the thermodynamic coefficients takes place in this process.

Methods

In order to calculate the isobaric exapansivity α_p and isothermal compressibility κ_T, we use the approximation of the volumetric data by our new equation of state (eq. (9) in Ref. 53) for glibenclamide (GLB)[33], verapamil hydrochlorine (VH)[54], carvedilol base (CB), ibuprofen (IBP), indometacin (IND), N,N-dimethyl-3-methylbenzamide (DEET) (all in Ref. 55), polystyrene (PS)[56], and polyvinylacetate (PVAc)[53]. The values of isothermal, isochoric and isobaric fragilities are estimated from temperature-volume version[40] of the entropic Avramov model[57], which are earlier reported for GLB, VH, CB, IND, IBP, DEET, PVAc (all in Ref. 55). The isobaric heat capacity data for GLB (also reported in Ref. 33), VH, CB, IBP, IND, and DEET have been measured at ambient pressure by using the differential scanning calorimetery with stochastic temperature modulation (TOPEM), whereas literature reports on $C_p(T)$ at $p = 0.1\,MPa$ for PS[56], PVAc[58], have been used. It also may be of value to mention that the determination of the total entropy is not required to calculate the values of dT_g/dpaccording to equation (7) since the total entropy can be expressed by the well-known thermodynamic formula, $S(T, p) = S_r + \int_{T_r}^{T} C_p(T, p_r)/TdT - \int_{p_r}^{p} (\partial v(T, p)/\partial T)_p dp$, where $S_r = S(T_r, p_r)$ is the constant entropy of the reference state (which can be defined by the glass transition temperature at ambient pressure) and then S_r can be omitted for estimation $(\partial S/\partial v)_\tau$.

References

1. Hensel-Bielowka, S., Ziolo, J., Paluch, M. & Roland, C. M. The effect of pressure on the structural and secondary relaxations in 1,1′-bis(p-methoxyphenyl) cyclohexane. *J. Chem. Phys.* **117,** 2317–2323 (2002).
2. Casalini, R., Paluch, M. & Roland, C. M. Dynamics of Salol at elevated pressure. *J. Phys. Chem. A* **107,** 2369–2373 (2003).
3. Pawlus, S., Paluch, M., Ziolo, J. & Roland, C. M. On the pressure dependence of the fragility of glicerol. *J. Phys.: Condens. Matter* **21,** 332101-1-3 (2009).
4. Paluch, M., Pawlus, S., Grzybowski, A., Grzybowska, K., Wlodarczyk, P. & Ziolo, J. Fragility versus activation volume: insight into molecular dynamics of glass-forming hydrogen-bonded liquids. *Phys. Rev. E* **84,** 052501-1-5 (2011).
5. Prigogine, I. & Defay, R. Chemical thermodynamics, Chap. 9; Longmans Green, New York, (1954).
6. Hirai, N. & Eyring, H. Bulk viscosity of polymeric systems. *J. Polym. Sci.* **37,** 51–70 (1959).
7. Schmelzer, J. W. P. Kinetic criteria of glass formation and the pressure dependence of the glass transition temperature. *J. Chem. Phys.* **136,** 074512-1-11 (2012).
8. Goldstein, M. & Simha, R. Introduction *Ann. N. Y. Acad. Sci.* **279** 1–1 (1979).
9. Angell, C., A. & Sichina, W. Thermodynamics of the glass transition: empirical aspects. *Ann. N.Y. Acad. Sci.* **279,** 53–67 (1976).
10. Davies, R. O. & Jones G. O. The irreversible approach to equilibrium in glasses. *Proc. R. Soc. London, Ser. A* **217,** 26–42 (1953).
11. de Donder, Th. & van Rysselberghe, P. *Thermodynamic Theory of Affinity*. (Stanford University Press, 1936).
12. Simon, F. Über den Zustand der unterkühlten Flüssigkeiten und Gläser. *Z. Anorg. Allg. Chem.* **203,** 219–227 (1931).
13. Hutchinson, J. M. & Kovasc, A. J. Proceedings of the Symposium on the Structure of Non-Crystalline Materials, edited by P. H. Gaskell. *Society of Glass Technology, Cambridge*, **167** (1977).
14. Davies, R. O. & Jones, G. O. Thermodynamic and kinetic properties of glasses. *Adv. Phys.* **2,** 370–410 (1953).
15. Goldstein, M. Viscous liquids and the glass transition. IV. Thermodynamic equations and the transition. *J. Phys. Chem.* **77,** 667–673 (1973).
16. Goldstein, M. Some thermodynamic aspects of the glass transition: free volume, entropy, and enthalpy theories. *J. Chem. Phys.* **39,** 3369–3374 (1963).
17. O'Reilly, J. M. The effect of pressure on glass temperature and dielectric relaxation time of polyvinyl acetate. *J. Polym. Sci.* **57,** 429–444 (1962).
18. Naoki, M., Matsumoto, K. & Matsushita, M. Factors determining relaxation time and glass transition. 2. Triphenylchloromethane/o-terphenyl mixture. *J. Phys. Chem.* **90,** 4423–4427 (1986).
19. Nieuwenhuizen, Th. M. Ehrenfest relations at the glass transition: solution to an old paradox. *Phys. Rev. Lett.* **79,** 1317–1320 (1997).
20. McKenna, G. B. A brief discussion: Thermodynamic and dynamic fragilities, non-divergent dynamics and the Prigogine-Defay ration. *J. Non-Cryst. Solids* **355,** 663–671 (2009).
21. Casalini, R., Gamache R. F. & Roland, C. M. Density-scaling and the Prigogine-Defay ratio in liquids. *J. Chem. Phys.* **135,** 224501-1-5 (2011).
22. Angel, C. A. & Klein, I. S. Prigogine and Defay say relax. *Nature Phys.* **7,** 750–751 (2011).
23. Schmelzer, J. W. & Gutzow, I. The Prigogine-Defay ratio revisited. *J. Chem. Phys.* **125,** 184511-1-11 (2006).
24. Gutzow, I. S. & Schmelzer J. W. P. *The vitreous state: thermodynamics, structure, rheology*. (Springer, 2013).
25. Jones, G. O. Viscosity and related properties in glass. *Rep. Prog. Phys.* **12,** 133–162 (1949).
26. Sanditov, B. D. & Sangadiev, S. Sh. & Sanditov, D. S. Relaxation time and cooling rate of a liquid in the glass transition range. *Glass Phys. Chem.* **33,** 445–454 (2007).
27. Schmelzer, J. W. P. & Gutzow, I. S. *Glasses and the glass transition*. (WILEY-VCH, 2011).
28. Ritland, H. N. Density phenomena in the transformation range of a borosilicate crown glass. *J. Am. Ceram. Soc.* **37,** 370–377 (1954).
29. Moynihan, C. T., Easteal, A. J., Wilder, J. & Tucker, J. Dependence of the glass transition temperature on heating and cooling rate. J. *Phys. Chem.* **78,** 2673–2677 (1974).
30. Moynihan, C. T., Easteal, A. J., De Bolt, M. A. & Tucker, J. Dependence of the fictive temperature of glass on cooling rate. *J. Am. Ceram. Soc.* **59,** 12–16 (1976).
31. Mazurin, O. V. Problems of compatibility of the values of glass transition temperatures published in the world literature. *Glass Phys. Chem.* **33,** 22–36 (2007).
32. Hodge, I. M. Enthalpy relaxation and recovery in amorphous materials. *J. Non-Cryst. Solids* **169,** 211–266 (1994).
33. Koperwas, K. *et al.* Pressure coefficient of the glass transition temperature in the thermodynamic scaling regime. *Phys. Rev. E* **86,** 041502-1-6 (2012).
34. Grzybowska, K., Grzybowski, A., Pawlus, S., Pionteck, J. & Paluch, M. Role of entropy in the thermodynamic evolution of the time scale of molecular dynamics near the glass transition. *Phys. Rev. E* **91,** 062305-1-13 (2015).
35. Floudas, G., Paluch, M., Grzybowski, A. & Ngai, K. L. *Molecular Dynamics of Glass-Forming Systems: Effects of Pressure* (Springer, 2011).

36. Casalini, R. & Roland, C. M. Determination of the thermodynamic scaling exponent for relaxation in liquids from static ambient-pressure quantities. *Phys. Rev. Lett.* **113,** 085701-1-5 (2014).
37. Gundermann, D. *et al.* Predicting the density-scaling exponent of a glass-forming liquid from Prigogine–Defay ratio measurements. *Nature Phys.* **7,** 816–821 (2011).
38. Roland, C. M., Hansel-Bielowka, S., Paluch, M. & Casalini, R. Supercooled dynamics of glass-forming liquids and polymers under hydrostatic pressure. *Rep. Prog. Phys.* **68,** 1405- 1478 (2005).
39. Paluch, M. *et al.* A Relationship between intermolecular potential, thermodynamics, and dynamic scaling for a supercooled ionic liquid. *J. Phys. Chem Lett.* **1,** 987–992 (2010).
40. Casalini, R., Mohanty, U. & Roland, C. M. Thermodynamic interpretation of the scaling of the dynamics of supercooled. *J. Chem. Phys.* **125,** 014505-1-9 (2006).
41. Roland, C. M., Bair, S. & Casalini, R. Thermodynamic scaling of the viscosity of van der Waals, H-bonded, and ionic liquids. *J. Chem. Phys.* **125,** 124508-1-8 (2006).
42. Pedersen, U. R., Bailey, N. P., Schrøder, T. B. & Dyre, J. C. Strong pressure-energy correlations in van der Waals liquids. *Phys. Rev. Lett.* **100,** 015701-1-4 (2008).
43. Bailey, N. P., Pedersen, U. R., Gnan, N., Schrøder, T. B. & Dyre, J. C. Pressure-energy correlations in liquids. I. Results from computer simulations. *J. Chem. Phys.* **129,** 184507-1-13 (2008).
44. Bailey, N. P., Pedersen, U. R., Gnan, N., Schrøder, T. B. & Dyre, J. C. Pressure-energy correlations in liquids. II. Analysis and consequences. *J. Chem. Phys*. **129,** 184508-1-20 (2008).
45. Coslovich, D. & Roland, C. M. Thermodynamic scaling of diffusion in supercooled Lennard-Jones liquids. *J. Phys. Chem. B* **112,** 1329–1332 (2008).
46. Coslovich, D. & Roland, C. M. Pressure-energy correlations and thermodynamic scaling in viscous Lennard-Jones liquids. *J. Chem. Phys.* **130,** 014508-1-5 (2009).
47. Grzybowski, A.; Koperwas, K. & Paluch, M. Scaling of volumetric data in model systems based on the Lennard-Jones potential. *Phys. Rev. E* **86,** 031501-1-9 (2012).
48. Kreul, G. H., Urban, S. & Wurflinger, A. Dielectric studies of liquid crystals under high pressure: Static permittivity and dielectric relaxation in the nematic phase of pentylcyanobiphenyl (5CB). *Phys. Rev. A* **45,** 8624–8631 (1992).
49. Urban, S. & Wurflinger, A. Dielectric properties of liquid crystals under high pressure. *Adv. Chem. Phys.* **98,** 143–216 (1997).
50. Bruckert, T., Wurflinger, A. & Urban, S. Dielectric studies on liquid crystals under high pressure: V. Static permittivity and low frequency relaxation process in 4-n-heptyl-4'-cyanobiphenyl (7CB). *Ber. Bunsengens. Phys. Chem.* **97,** 1209–1212 (1993).
51. Tarnacka, M. *et al.* Thermodynamic scaling of molecular dynamics in supercooled liquid state of pharmaceuticals: Itraconazole and ketoconazole. *J. Chem. Phys*. **142,** 224507-1-8 (2015).
52. Roland, C. M. *et al.* Thermodynamic scaling and the characteristic relaxation time at the phase transition of liquid crystals. *J. Chem. Phys.* **128,** 224506-1-9 (2008).
53. Grzybowski, A., Grzybowska, K., Paluch, M., Swiety, A. & Koperwas, K. Density scaling in viscous systems near the glass transition. *Phys. Rev. E* **83,** 041505-1-7 (2011).
54. Wojnarowska, Z. *et al.* Study of molecular dynamics of pharmaceutically important protic ionic liquid-verapamil hydrochloride. I. Test of thermodynamic scaling. *J. Chem, Phys.* **131,** 104505-1-14 (2009).
55. Koperwas, K., Grzybowski, A., Grzybowska, K., Wojnarowska, Z. & Paluch, M. In search of correlations between the four-point measure of dynamic heterogeneity and other characteristics of glass-forming liquids under high pressure. *J. Non-Cryst. Solids*, **407,** 196–205 (2015).
56. Barry, S. Untersuchung des Glasübergangs von Polystyrol mit der Druckdilatometrie. *Ph.D. thesis*, The Ulm Univeristy, Germany, (1992).
57. Avramov, I. Pressure dependence of viscosity of glassforming melts. *J. Non-Cryst. Solids* **262,** 258–263 (2000).
58. Heinrich, W. & Stoll, B. Description of the freezing-in process in poly(vinyl acetate) based on the meander model. *Progr. Colloid Polym. Sci*. **78,** 37–53 (1988).
59. Wojnarowska, Z. *et al.* Broadband dielectric relaxation study at ambient and elevated pressure of molecular dynamics of parmaceutical: indomethacin. *J. Phys. Chem. B* **113,** 12536–12545 (2009).
60. Adrjanowicz, K. *et al.* Dielectric relaxation and crystallization kinetics of ibuprofen at ambient and elevated Pressure. *J. Phys. Chem. B* **114,** 6579–6593 (2010).

Acknowledgements

The authors are grateful for the financial support from the Polish National Science Center based on Decision No. DEC-2012/04/A/ST3/00337 within the program MAESTRO 2.

Author Contributions

K.K. performed the mathematical calculations and data analysis as well as wrote the main manuscript text. S.N.T. contributed to the writing of the manuscript. E.M., A.G. and M.P. supervised the mathematical calculations, data analysis and discussed the results. All authors reviewed the manuscript.

Additional Information

Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Koperwas, K. *et al.* Thermodynamic consequences of the kinetic nature of the glass transition.. *Sci. Rep.* **5**, 17782; doi: 10.1038/srep17782 (2015).

5. OMÓWIENIE POZOSTAŁYCH OSIĄGNIĘĆ NAUKOWO-BADAWCZYCH

Efektem pracy naukowej, prowadzonej przeze mnie w okresie studiów doktoranckich są publikacje A1-A4. Przyczyniła się ona również do powstania sześciu innych artykułów naukowych (B1-B6), opublikowanych w czasopismach znajdujących się na liście filadelfijskiej.

Podczas omawiania zagadnienia skalowania gęstościowego w rozdziale 3.1, wspomniałem o sugerowanym w literaturze połączeniu pomiędzy wykładnikiem skalującym γ a wykładnikiem części potencjału międzymolekularnego, która opisuje odziaływania odpychające. Związek pomiędzy powyższymi wielkościami został potwierdzony w artykule B2 na przykładzie trzech modelowych układów typu Koba-Andersena, w których odziaływania międzycząsteczkowe opisane zostały potencjałami: Lennarda-Jonesa oraz odwrotnego prawa potęgowego o wykładniku 15 i 18. Ponadto w publikacji potwierdzono słuszność wcześniej zaproponowanego równania (rów. 12 w Ref. 31) łączącego γ z parametrem (γ_{EOS}) równania stanu (rów. 9 w Ref. 32), które zostało wyprowadzone bezpośrednio z potencjału międzymolekularnego i z sukcesem sprawdzone dla wielu substancji w pobliżu przejścia szklistego[32]. Należy jednak zaznaczyć, że stosowalność powyższego równania jest ograniczona tylko i wyłącznie do warunków termodynamicznych, w których izotermiczny moduł ściśliwości jest liniową funkcją ciśnienia oraz, że zostało ono wyprowadzone dla potencjału międzycząsteczkowego opisanego odwrotnym prawem potęgowym. Powyższe ograniczenia, jak również zaobserwowana w artykule B2 zależność wykładnika

skalującego od gęstości, stały się motywacją do dalszego rozwijania równania stanu. W artykule B6, wykorzystując zaproponowaną przez prof. J. Dyrego i współautorów teorię izomorfów[33,34], wyprowadzono z potencjału międzymolekularnego nowe równanie stanu, które jest wolne od ograniczenia narzuconego przez liniową zależność izotermicznego modułu ściśliwości od ciśnienia. Dzięki temu może być stosowane w znacznie większym zakresie ciśnień lub gęstości, co zostało pokazane dla modelowego układu Koba-Andersena (artykuł B6).

Badana przeze mnie dynamiczna heterogeniczność układów w pobliżu przejścia szklistego jest również tematem publikacji naukowych: B1, B4 i B5. W artykule B1, na podstawie dwóch typowych substancji formujących szkła, została przeprowadzona analiza zmian stopnia dynamicznej heterogeniczności podczas doprowadzania układu do stanu szklistego w warunkach izobarycznych, izotermicznych i izochorycznych. Wyniki zaprezentowane w omawianym artykule wyraźnie pokazują, że temperatura wywiera większy wpływ na liczbę dynamicznie skorelowanych molekuł niż ciśnienie (jeśli porównujemy efekty obu wyżej wymienionych wielkości termodynamicznych w funkcji czasu relaksacji strukturalnej). Sprawia to, że ciśnienie i temperatura nie mogą być traktowane jak dwie równorzędne wielkości termodynamiczne. Układ doprowadzany do przejścia szklistego za pomocą kompresji izotermicznej staje się bardziej homogeniczny niż ten doprowadzany do T_g za pomocą izobarycznego ochładzania. Artykuł B4, poświęcony jest szczegółowej analizie wkładów do stopnia dynamicznej heterogeniczności pochodzących od fluktuacji entalpii, temperatury i gęstości. Na przykładzie trzech cieczy typu van der Waalsa wykazano, że wkład pochodzący od fluktuacji entalpii jest w przybliżeniu równy sumie wkładów pochodzących od fluktuacji gęstości i temperatury. Pokazano również, że fluktuacje temperatury wpływają w większym stopniu na stopień dynamicznej heterogeniczności

niż fluktuacje gęstości. Wyniki opublikowane w artykule B4 sugerują, że wzrost ciśnienia w warunkach izochronicznych powoduje homogenizację układu. Rezultat ten jest szczególnie interesujący, ponieważ kształt widm dielektrycznych w analizowanych warunkach izochronicznych pozostaje niezmieniony, co świadczy o braku korelacji pomiędzy ilością dynamicznie skorelowanych molekuł a parametrami funkcji opisującej relaksację strukturalną – funkcji odpowiedzi. Wynik ten stał się motywacją badań ukierunkowanych na analizę połączenia stopnia dynamicznej heterogeniczności i relaksacji strukturalnej w kontekście obserwowanego dla niej skalowania gęstościowego. Efekty powyższej analizy zostały opublikowane w artykule B5, w którym zapostulowano, a następnie pokazano potęgowe skalowanie gęstościowe stopni dynamicznej heterogeniczności, $\left(\chi_4\right)^{\max} = f\left(T\upsilon^{\gamma_\chi}\right)$. Następnie dowiedziono, że czas relaksacji strukturalnej nie może być w ogólności funkcją tylko i wyłącznie stopnia dynamicznej heterogeniczności. Należy zaznaczyć, że bezpośrednia zależność pomiędzy badanymi wielkościami była sugerowana w literaturze. Ponadto w artykule pokazano, że w przypadku gdy potęgowe skalowanie gęstościowe jest słuszne przynajmniej z dobrym przybliżeniem, dodatkowa zmienna łącząca stopień dynamicznej heterogeniczności i czas relaksacji strukturalnej powinna być tylko i wyłącznie potęgową funkcją gęstości $\rho^{\Delta\gamma}$, gdzie $\Delta\gamma = \gamma - \gamma_\chi$ jest miarą rozbieżności pomiędzy τ a $\left(\chi_4\right)^{\max}$.

Wyniki moich prac badawczych poświęconych objętości aktywacji zostały wykorzystane w artykule B3, w którym wyprowadzono izotermiczne równanie stanu dla objętości aktywacji, słuszne w warunkach liniowej zależności izotermicznego modułu ściśliwości objętości aktywacji od ciśnienia. Przedstawiona analiza danych eksperymentalnych ujawniła, że powyższe ograniczenie jest spełnione dla pięciu

rzeczywistych i jednej modelowej substancji. Ponadto wykazała, że izotermiczny moduł ściśliwości objętości aktywacji, maleje wraz ze wzrostem ciśnienia. Dodatkowo, wykorzystując potęgowe skalowanie gęstościowe, w artykule rozszerzono wyprowadzone wcześniej izotermiczne równanie stanu i uzyskano formułę, która jak wykazała analiza rzeczywistych i modelowych substancji, poprawnie opisuje zależność objętości aktywacji od ciśnienia i temperatury. Warto dodać, że przebadane substancje należały do różnych grup materiałowych (cieczy typu van der Waals'a, polimerów, substancji jonowych i substancji z silną tendencją do forowania wiązań wodorowych). Odwrotnie proporcjonalna zależność izotermicznego modułu ściśliwości objętości aktywacji od ciśnienia została wyjaśniona poprzez wyprowadzoną współzależność pomiędzy współczynnikiem liniowym (γ_{act}) powyższej zależności, wykładnikami skalującym objętości właściwe (γ_{EOS}) oraz czasy relaksacji strukturalnej (γ) i parametrem temperaturowo-objętościowej wersji[35] entropowego modelu użytego do opisania zachowania czasów relaksacji[36].

6. PODSUMOWANIE

Niniejszą rozprawę doktorską stanowi seria artykułów naukowych poświęconych ciśnieniowemu współczynnikowi temperatury przejścia szklistego i relacji pomiędzy wielkościami termodynamicznymi w przejściu szklistym. Punktem wyjścia dla przeprowadzonych badań jest definicja przejścia szklistego poprzez ustaloną wartość czasu relaksacji strukturalnej. Wykorzystując aktualnie szeroko eksploatowany w literaturze pomysł skalowania gęstościowego, w artykule A1, zaprezentowałem oraz z sukcesem eksperymentalnie zweryfikowałem nowy wzór opisujący ciśnieniowy współczynnik temperatury przejścia szklistego. Może być on wykorzystany do wyprowadzenia współzależności pomiędzy wielkościami termodynamicznymi w przejściu szklistym, która byłaby alternatywą do fundamentalnej w literaturze relacji Prigogine'a-Defaya (relacja Prigogine'a-Defaya nie jest poprawna w przejściu szklistym). Jednakże, wyniki kolejnych przeprowadzonych przeze mnie badań pokazują, że definiując przejście szkliste wyłącznie poprzez ustaloną wartość czasu relaksacji strukturalnej, nie jest możliwym wyprowadzenie dwóch niezależnych wzorów opisujących ciśnieniowy współczynnik temperatury przejścia szklistego. Tym samym na podstawie wyłącznie izochronicznej definicji przejścia szklistego, nie można otrzymać szukanej współzależności pomiędzy wielkościami termodynamicznymi w przejściu szklistym (artykuł A4). Niemniej jednak omawiana relacja może być uzyskana po wprowadzeniu dodatkowego (innego niż izochroniczny) warunku spełnionego w przejściu szklistym. Przeprowadzone badania zależności relaksacji strukturalnej od makroskopowych wielkości termodynamicznych sugerują, że istnienia dodatkowego warunku spełnionego w przejściu szklistym należy poszukiwać

w szczególności we właściwościach mikroskopowych substancji, np. tzw. dynamicznej heterogeniczności. Dlatego w artykule A2, wykorzystałem sugerowaną w literaturze współzależność pomiędzy wkładami do stopnia dynamicznej heterogeniczności pochodzącymi od fluktuacji entalpii, temperatury i gęstości. Na jej podstawie wyprowadziłem niezależny wzór opisujący ciśnieniowy współczynnik temperatury przejścia szklistego, a następnie otrzymałem relację pomiędzy wielkościami termodynamicznymi w przejściu szklistym, która jest alternatywą do relacji Prigogine'a-Defaya. Należy podkreślić, że teoretyczne przewidywania zaproponowanej przeze mnie formuły są zgodne z wynikami ich eksperymentalnej weryfikacji. Z uwagi na fakt, że wykorzystane przeze mnie estymaty stopnia dynamicznej heterogeniczności bazują na analizie czasów relaksacji strukturalnej, zbadałem korelację pomiędzy stopniem dynamicznej heterogeniczności a innymi wielkościami otrzymywanymi z analizy relaksacji strukturalnej (objętością aktywacji, izobaryczną i izochoryczną kruchością). Przeprowadzone badania wykazały, że stopień dynamicznej heterogeniczności jest niezależny od objętości aktywacji oraz różnicy pomiędzy izobaryczną i izochoryczną kruchością (artykuł A3). Oznacza to iż, współzależności pomiędzy wkładami do stopnia dynamicznej heterogeniczności, która umożliwiła otrzymanie relacji pomiędzy wielkościami termodynamicznymi w przejściu szklistym, nie może być w prosty sposób zastąpiona poprzez dowolną zależność wynikającą z analizy czasów relaksacji strukturalnej.

Podsumowując, cel badań przedstawionych w niniejszej rozprawie doktorskiej, jakim było zaproponowanie relacji pomiędzy wielkościami termodynamicznymi podczas przejścia szklistego, został w pełni osiągnięty. Teoretyczne przewidywania wyprowadzonej współzależności są zgodne z wynikami analizy danych eksperymentalnych. Ponadto przeprowadzone badania wykazały, że do otrzymania

omawianej współzależności niezbędny jest dodatkowy, inny niż izochroniczny, warunek spełniony w przejściu szklistym, którego przykładowa postać została przeze mnie zaproponowana.

7. BIBLIOGRAFIA

1. I. Prigogine and R. Defay, Chemical Thermodynamics (Longmans Green, New York, 1954), Chap. 9.
2. N. Hirai and H. Eyring, J. Polym. Sci. 37, 51 (1959).
3. J. W. P. Schmelzer, J. Chem. Phys. 136, 074512 (2012).
4. Th. de Donder and P. van Rysselberghe, Thermodynamic Theory of Affinity (Stanford University Press, Stanford, 1936).
5. F. Simon, Z. Anorg. Allg. Chem. 203, 219 (1931).
6. R. O. Davis, G. O. Jones, Proc. R. Soc. London, Ser. A 217, 26 (1953).
7. C. A. Angel, I. S. Klein, Nature Phys. 7, 750 (2011).
8. J. W. Schmelzer, I. Gutzow, J. Chem. Phys. 125, 184511 (2006).
9. G. O. Jones, Rep. Prog. Phys. 12, 133 (1949).
10. G. M. Bartenev, Dokl. Akad. Nauk SSSR 69, 373 (1949).
11. G. M. Bartenev, Dokl. Akad. Nauk SSSR 76, 227 (1951).
12. G. M. Bartenev and I. A. Lukyanov, Zh. Fiz. Khim. 29, 1486 (1955).
13. H. N. Ritland, J. Am. Ceram. Soc. 37, 370 (1954).
14. C. T. Moynihan, A. J. Easteal, J. Wilder, J. Tucker, J. Phys. Chem. 78, 2673 (1974).
15. C. T. Moynihan, A. J. Easteal, M. A. DeBolt, J. Tucker, J. Am. Ceram. Soc. 59, 12 (1976).
16. O. V. Mazurin, Glass Phys. Chem. 33, 22 (2007).
17. M. Hodge, J. Non-Cryst. Solids 169, 211 (1994).
18. G. Adam and J. H. Gibbs, J. Chem. Phys. 43, 139 (1965).
19. L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hoˆte, F. Ladieu, M. Pierno, Science 310, 1797 (2005).

20. C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hoˆte, G. Tarjus, Phys. Rev. E 76, 041510 (2007).

21. L. Hong, P. D. Gujrati, V. N. Novikov, A. P. Sokolov, J. Chem. Phys. 131, 194511 (2009).

22. L. Hong, V. N. Novikov, A. P. Sokolov, Phys. Rev. E .83, 061508 (2011).

23. L. Hong, V. N. Novikov, A. P. Sokolov, J. Non-Cryst. Solids 357, 351 (2011).

24. W. Schirmacher, B. Schmid, C. Tomaras, G. Viliani, G. Baldi, G. Ruocco, T. Scopigno, Phys. Status Solidi C 5, 862 (2008).

25. E. Duval, A. Boukenter, T. Achibat, J. Phys. Condens. Matter 2, 10227 (1990).

26. A. P. Sokolov, A. Kisliuk, M. Soltwisch, D. Quitmann, Phys. Rev. Lett. 69, 1540 (1992).

27. S. R. Elliott, Europhys. Lett. 19, 201 (1992).

28. A. P. Sokolov, R. Calemczuk, B. Salce, A. Kisliuk, D. Quitmann, E. Duval, Phys. Rev. Lett. 78, 2405 (1997).

29. R. Casalini, M. C. Roland, Phys. Rev. Lett. 113, 085701 (2014).

30. J. W. P. Schmelzer, T. W. Tropin, J. Non-Cryst. Solids 407, 170 (2015).

31. M. Paluch, S. Haracz, A. Grzybowski, M. Mierzwa, J. Phys. Chem. Lett. 1, 987 (2010).

32. A. Grzybowski, K. Grzybowska, M. Paluch, A. Swiety, K. Koperwas, Phys. Rev. E 83, 041505 (2011).

33. N. Gnan, T. Schroder, U. Pedersen, N. Bailey, J. Dyre, J. Chem. Phys. 131, 234504 (2009).

34. T. Schroder, N. Gnan, U. Pedersen, N. Bailey, J. Dyre, J. Chem. Phys. 134, 164505 (2011).

35. R. Casalini, U. Mohanty, C. M. Roland, J. Chem. Phys. 125, 014505 (2006).

36. I. Avramov, J. Non-Cryst. Solids 262, 258 (2000).

8. MATERIAŁY DODATKOWE

Poniżej przedstawione materiały dodatkowe stanowią uzupełnienie artykułów A2 i A4 zaprezentowanych w rozdziale 4.

8.1. MATERIAŁY UZUPEŁNIAJĄCE ARTYKUŁ A2

1. A determination of the relaxation time corresponding to the glass transition for Carvedilol Base

In the main text, we present the method of analysis of volumetric data for determining the glass transition temperature at selected pressure. According to general wisdom, the glass transition is considered as a kinetic process and it can be defined as a state at which the structural relaxation time τ achieves some characteristic value [1]. As we show in the inset in Fig. 1 in the main text, both methods for determining the pressure dependence of the glass transition temperature give consistent results. In this paragraph, we present the method for determining the structural relaxation time corresponding to the glass transition for Carvedilol Base CB. From dielectric spectroscopy measurements, we obtained the temperature-pressure dependence of structural relaxation times. Using an equation of state [2], which describes the temperature-pressure dependence of specific volume $v(T,p)$ (appropriate parameters are reported in Ref. [3] for CB), we received the temperature-volume dependence of structural relaxation times $\tau(T,v)$. The latter was approximated by the temperature-volume version [4] of the Avramov entropic model [5] (see Ref. [3]), which enabled us to estimate the structural relaxation time for each pair of the glass transition volume and temperature obtained from the analysis of volumetric measurements. Our study revealed that the glass transition for CB occurs at a constant structural relaxation time, the decimal logarithm of which equals 1.625.

Taking this observation into account, we supplemented the experimental dependence of the glass transition temperatures on pressure (the inset in Fig. 1 in the main text) with four points, which come from high pressure dielectric spectroscopy measurements, see Fig. S.1.

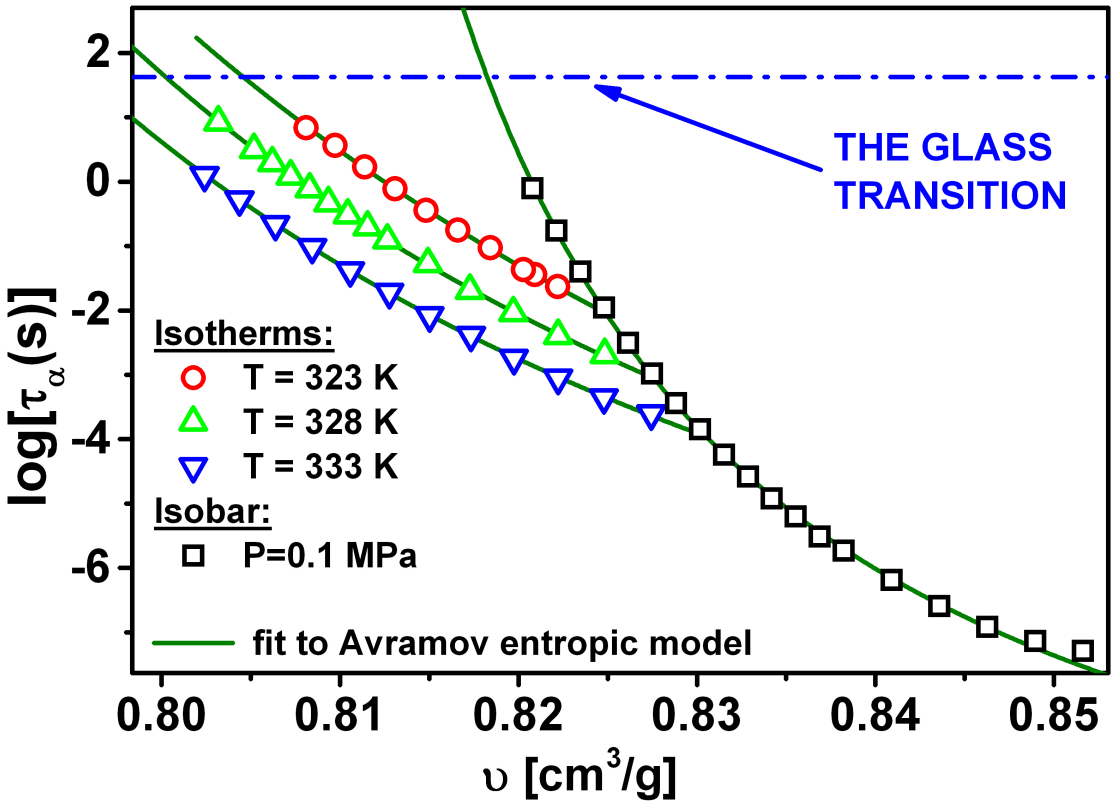


Fig. S.1

Plot of isothermal and isobaric measurements of structural relaxation times for CB. The solid lines are fitted to the experimental data by using the temperature-volume version of entropic Avramov model [5] with the earlier reported parameters [3]. The dash-dotted line reflects the dynamic state (defined by a characteristic structural relaxation time), which corresponds to the glass transition.

2. The density scaling of structural relaxation times for Carvedilol Base

Since the linear dependence of $\log(T)$ on $\log(v)$ has been revealed for many systems at a constant structural relaxation time, the density scaling of structural relaxation times is

expected to have the following form $\tau = F\left(T\upsilon^{\gamma}\right)$, and γ can be easily estimated from the isochronal dependence $\log(T) = -\gamma\log(\upsilon) + C$, where $C = const$ at $\tau = const$.

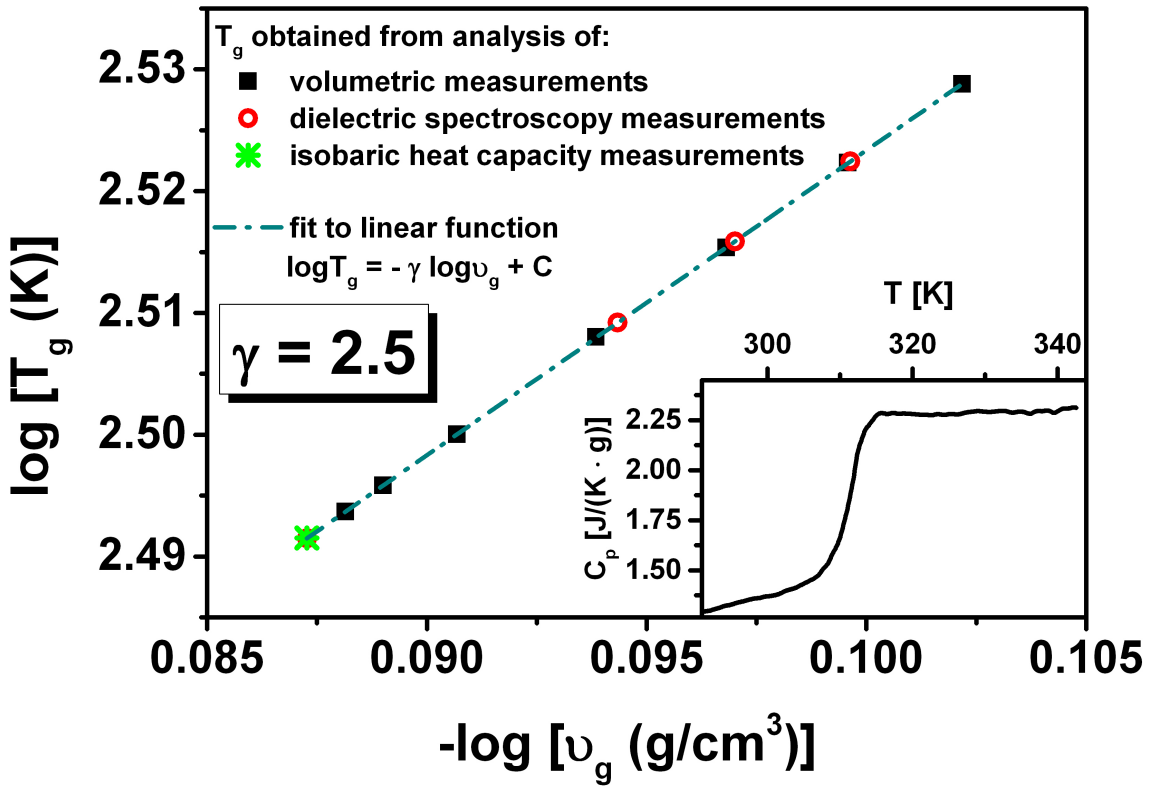


Fig. S.2

Plot of the dependence of logarithm of the glass transition temperatures on logarithm of the glass transition volumes, which are obtained from the analysis of volumetric, dielectric, and isobaric heat capacity measurements for CB. The dash-dotted line reflects the linear dependence of $\log\left(T_g\right)$ on $\log\left(\upsilon_g\right)$. The slope of the linear dependence is identified with the scaling exponent γ. In the inset, the temperature dependence of the isobaric specific heat near the glass transition at ambient pressure are presented for CB.

Additionally, in Fig. S.2 we added a value of the glass transition temperature determined from the analysis of the temperature dependence of isobaric heat capacity measured at ambient pressure by the differential scanning calorimetry with stochastic temperature modulation (TOPEM), see the inset in Fig. S.2. It is worth noting that the above

value of T_g very well corresponds to the glass transition temperatures obtained from volumetric and dielectric spectroscopy measurements. Our analysis of the linear dependence of $\log(T_g)$ on $\log(\upsilon_g)$ resulted in the value of $\gamma = 2.5$, which enables a very well density scaling of the structural relaxation times for CB, as one can see in Fig. S.3.

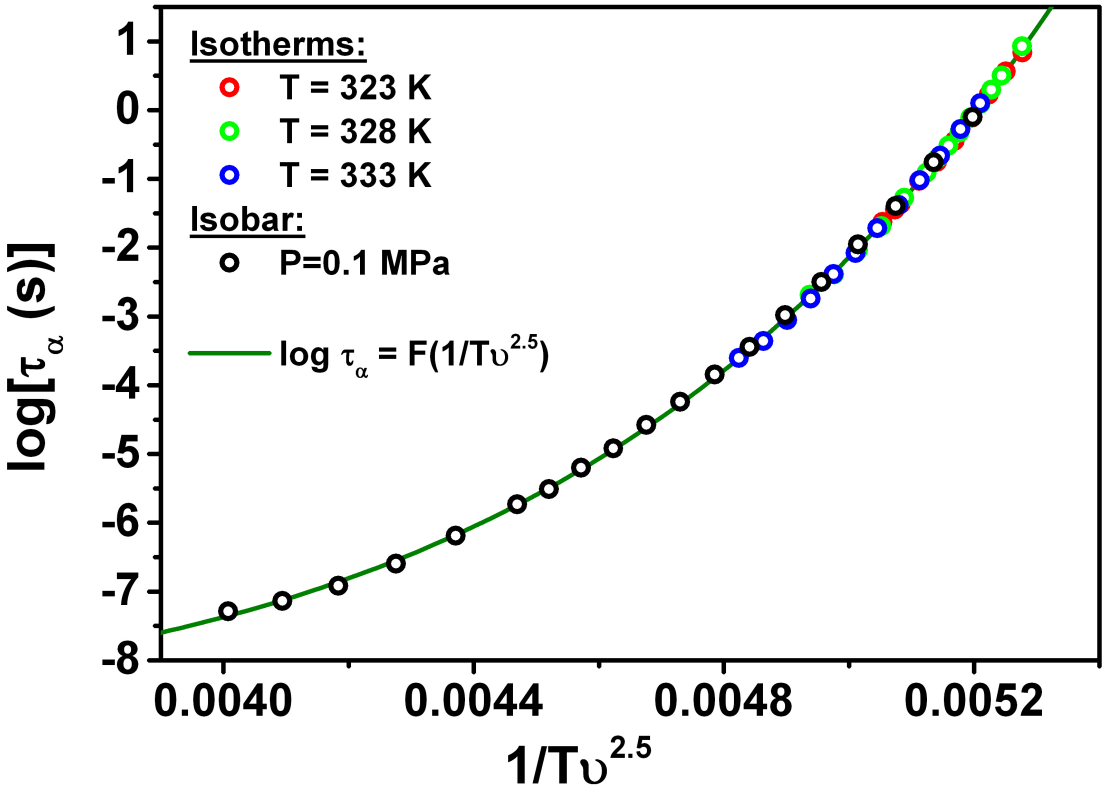


Fig. S.3

Plot of the density scaling of three experimental isotherms and isobar of structural relaxation times determined from the broadband dielectric spectroscopy measurements of CB, where the scaling exponent $\gamma = 2.5$. The solid line represents the fit of experimental data to the temperature-volume version of entropic Avramov model [5] with the earlier reported parameters [3].

3. Theoretical basis for estimation of the degree of the dynamic heterogeneity

Since the experimental measurements of higher order dynamic susceptibility is a very difficult task, a way to estimate $\chi_4(t)$ has been proposed by Berthier *et al.* [6,7], who

employed the ensemble-average two-point correlators $C(t,0)=\delta O(t)\delta O(0)$, where δO is the instantaneous value of the fluctuation of some observable O (e.g. density) from its average $\langle O\rangle$. The standard experimental researches of liquids dynamics give access to average values of aforementioned correlator $\langle C(0,t)\rangle$ e.g. orientational correlation function accessible in dielectric spectroscopy experiment. The information of amplitude of $C(0,t)$ fluctuations around its mean value is given by variance $\left\langle \left(C(0,t)-\langle C\rangle\right)^2\right\rangle$. Thus the variance informs about fluctuations of dynamics i.e. dynamic heterogeneity $\chi_4(t)=N\left\langle \left(C(0,t)-\langle C\rangle\right)^2\right\rangle$ (N is the total number of molecules in system). Unfortunately, the value of variance of $C(0,t)$ is not possible to obtain in standard spectroscopy methods. Nevertheless, experimentally viably method for analyzing space and time correlations in the glass forming liquids rely on inspection of the response of the average dynamics to an infinitesimal change in external parameter. In case of experimentally accessible NPT ensemble (from Cauchy-Schwarz inequality, which connects the spontaneous fluctuations of the dynamic and fluctuations of enthalpy, and thermodynamic relation $N\left\langle \left(H(0)-\langle H\rangle\right)^2\right\rangle_{NPT}=k_BT^2c_p$) one obtains $\chi_4^{NPT}(t)\geq\frac{k_BT^2}{c_p}\left(\chi_T^{NPT}\right)^2$, where $\chi_T^{NPT}=\left.\frac{\partial\langle C(0,t)\rangle}{\partial T}\right|_{N,P}=\frac{N}{k_BT^2}\left\langle \left(H(0)-\langle H\rangle\right)\left(C(0,t)-\langle C\rangle\right)\right\rangle_{NPT}$ is the three-point time dependent correlator, which estimates the spatial extend of the correlation between a fluctuation of enthalpy H at time 0 and at some point, and the change in the dynamics occurring at another point between time 0 and t. Thus it defines contribution to the dynamic heterogeneity induced by the fluctuations of enthalpy. On the other hand, under constant pressure conditions a change in the temperature is accompanied by change in the density. Therefore the effects of the temperature at constant density χ_T^{NVT} and the density at

constant temperature χ_ρ^{NPT} can be separated from the effect the enthalpy at NPT ensemble. Then one obtains another equation for lower bond of $\chi_4^{NPT} \geq \frac{k_B T^2}{c_\upsilon}\left(\chi_T^{NVT}\right)^2 + \rho^3 k_B T \kappa_T \left(\chi_\rho^{NPT}\right)^2$, where $\chi_n = \partial\left\langle C(t,0)\right\rangle / \partial n$ and n is a quantity, which triggers fluctuations contributing to the dynamic heterogeneity. It is worth mentioning that both inequality, which estimate lower bond of the χ_4^{NPT}, in general take forms $\chi_4^{NPT}(t) = \frac{k_B T^2}{c_p}\left(\chi_H^{NPT}\right)^2 + \chi_4^{NPH}$ and $\chi_4^{NPT} = \frac{k_B T^2}{c_\upsilon}\left(\chi_T^{NVT}\right)^2 + \rho^3 k_B T \kappa_T \left(\chi_\rho^{NPT}\right)^2 + \chi_4^{NVE}$. However χ_4^{NPH} and χ_4^{NVE} are expected to be small and positive number, therefore $\chi_4^{NPT}(t) \approx \frac{k_B T^2}{c_p}\left(\chi_T^{NPT}\right)^2 \approx \frac{k_B T^2}{c_\upsilon}\left(\chi_T^{NVT}\right)^2 + \rho^3 k_B T \kappa_T \left(\chi_\rho^{NPT}\right)^2$. According to Ref. 6 and 7 the maximum of dynamic susceptibility $(\chi_4)^{\max}$ yields directly to the number of dynamically correlated molecules or the size of the region within which the molecular dynamics is correlated, thus is the measure of the degree of the dynamic heterogeneity. By assuming that the correlation function used to estimate the induced fluctuations can be parameterized by Kohlrausch-Williams-Watts function $\Phi(t) = \exp\left[-(t/\tau_\alpha)^\beta\right]$, the expression for the maximum of the induced fluctuations takes a form $(\chi_n)^{\max} \approx \left(\frac{\partial\Phi(t)}{\partial x}\right|_{x=1}\left(\frac{\partial \ln \tau_\alpha}{\partial \ln n}\right)\frac{1}{n}$, where $x\left(=t/\tau_\alpha\right)$ equals 1 at $t = \tau_\alpha$, $\Phi'(1) = \beta / e$, and n is a thermodynamic variable such as p, T, and υ. Using the Kohlrausch-Williams-Watts function, Berthier *et al.* [6,7] derived the following equations for the degrees of the dynamic heterogeneity triggered by the fluctuations of enthalpy, temperature and density:

$$\left(\chi_4^H\right)^{\max} \approx \frac{k_B T^2}{\Delta c_p}\left(\frac{\beta}{e}\frac{\partial \ln \tau}{\partial T}\right|_p\Bigg)^2, \qquad \text{(S.1a)}$$

$$\left(\chi_4^T\right)^{\max} \approx \frac{k_B T^2}{\Delta c_v}\left(\frac{\beta}{e}\left.\frac{\partial \ln \tau}{\partial T}\right|_v\right)^2, \text{ and} \tag{S.1b}$$

$$\left(\chi_4^\rho\right)^{\max} \approx k_B T \kappa_T \rho^3\left(\frac{\beta}{e}\left.\frac{\partial \ln \tau}{\partial \rho}\right|_T\right)^2, \tag{S.1c}$$

where configurational values of the isobaric and isochoric heat capacities are employed to minimalize the contributions to the fluctuations, which are unrelated to the glassy dynamics. The suggested above mutual relation between contribution to the dynamic heterogeneity induced by the fluctuations of enthalpy, temperatures and density was confirmed for relationship between corresponding degrees of the dynamic heterogeneity for several van der Waals liquids at ambient and elevated pressures [7,8]. Summarizing, in the manuscript we use the four-point time dependent function estimated by exploiting the two-point time-dependent correlator that is accessible in the standard spectroscopy method.

4. Details of pressure coefficients of the glass transition temperature calculations

In order to test the predictions of our new formula for the pressure coefficient of the glass transition temperature as well as to compare the obtained result with the predictions of the Ehrenfest equations, we have examined CB and other fourteen glass forming liquids: ortho-Terphenyl (OTP), glibenclamide (GLB), polystyrene (PS), telmisartan (TLM), verapamil hydrochlorine (VH), glycerol (GLC), triethyl-2-acetylcitrate (TBAC), salol (SL), ibuprofen (IBP), indometacin (IND), cresolphthalein-dimethylether (KDE), polyvinylacetate (PVAc), N,N-dimethyl-3-methylbenzamide (DEET), and mixture of 67% o-terphenyl and 33% o-phenylphenol (OTP-OPP). Since all examined equations require calculations of $\alpha_p\left(T_g, p_g\right)$ and $\kappa_T\left(T_g, p_g\right)$ at the liquid state, we approximated volumetric data using our new equation of state (Eq. (9) in Ref. 2) for OTP [9] PS [10], VH [11], GLC [12], SL [13] or we used its earlier reported parameters for CB, IBP, IND, KDE, DEET (all in Ref [3]), GLB,

TLM (both in Ref [14]), PVAc [2], and TBAC [15]. In case of OTP-OPP, we took advantage of the temperature dependence of α_p and κ_T presented in Ref. [16]. The values of material dependent parameter γ were earlier reported for TLM [14], OTP-OPP [17], TBAC [15], CB, OTP, GLB, VH, GLC, IBP, IND, KDE, PVAc, and DEET (all in Ref. [3]), whereas for other materials we obtained them by using the fit of experimental data (reported in Ref [10] and [18] for Ps and SL, respectively) to the temperature-volume version of entropic Avramov model [5]. Eqs. (1b) and (3) require also determination of differences in isobaric and isochoric heat capacities between liquid and glassy states, ΔC_p and ΔC_v. The isobaric heat capacity data for CB (presented in inset of Fig. S.2), GLB (also reported in Ref. [14]), TLM, VH, SL, IBP, IND, DEET, TBAC have been measured at ambient pressure by using the differential scanning calorimetery with stochastic temperature modulation (TOPEM), whereas literature reports on $C_p(T)$ at $p = 0.1 MPa$ for OTP [19], PS [10], GLC [20], KDE [21], PVAc [22], OTP-OPP [16] ($p = 28.8 MPa$) have been exploited. Based on the well-known thermodynamic relation, $C_v = C_p - v T \alpha_p^2 / \kappa_T$, we have determined the dependence $C_v(T)$. The calculations of α_p and κ_T for the glass require the measurements of dependence $v(T,p)$ in the glassy state, which have not been performed for all examined materials, thus the number of materials for which we were able to estimate $\Delta\alpha_p$, $\Delta\kappa_T$, and ΔC_v has been limited.

[1] I. M. Hodge, J. Non-Cryst. Solids 169, 211 (1994).

[2] A. Grzybowski, K. Grzybowska, M. Paluch, A. Swiety, and K. Koperwas, Phys. Rev. E **83**, 041505 (2011).

[3] K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, and M. Paluch, J. Non-Cryst. Solids **407**, 196 (2015).

[4] R. Casalini, U. Mohanty, and C.M. Roland, J. Chem. Phys. **125**, 014505 (2006).

[5] I. Avramov, J. Non-Cryst. Solids **262**, 258 (2000).

[6] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hoˆte, F. Ladieu, and M. Pierno, Science **310**, 1797 (2005).

[7] C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hoˆte, and G. Tarjus, Phys. Rev. E **76**, 041510 (2007).
[8] K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, A. P. Sokolov, and M. Paluch, Phys. Rev. Lett. **111**, 125701 (2013).
[9] M. Naoki and S. Koeda, J. Phys. Chem. **93**, 948 (1989).
[10] S. Barry, Ph.D. thesis, The Ulm Univeristy, Germany, (1992).
[11] Z. Wojnarowska, M. Paluch, A. Grzybowski, K. Adrjanowicz, K. Grzybowska, K. Kaminski, P. Wlodarczyk, and J. Pionteck, J. Chem, Phys. **131**, 104505 (2009).
[12] A. Raiser, G. Kasper, and S. Hunklinger, Phys. Rev. B **72**, 094204 (2005); **74**, 019902(E) (2006).
[13] L. Comez, S. Corezzi, D. Fioretto, H. Kriegs, A. Best, and W. Steffen, Phys. Rev. E **70**, 011504 (2004).
[14] K. Koperwas, A. Grzybowski, K. Grzybowska, Z. Wojnarowska, J. Pionteck, A. P. Sokolov, and M. Paluch, Phys. Rev. E **86**, 041502 (2012).
[15] K. Grzybowska, A. Grzybowski, S. Pawlus, J. Pionteck, and M. Paluch, arXiv:1406.4563v3 [cond-mat.soft].
[16] S. Takahara, M. Ishikawa, O. Yamamuro, and T. Matsuo, J. Phys. Chem. B **103**, 792 (1999).
[17] M. Roland, S. Hansel-Bielowka, M. Paluch, and R. Casalini, rep. Prog. Phys. **68**, 1405 (2005).
[18] R. Casalini, M. Paluch, and C. M. Roland, J. Phys. Chem. A **107**, 2369 (2003).
[19] L. Comez, S. Corezzi, and D. Fiorento, Phil. Mag. **84**, 1521 (2004).
[20] O Sandberg, P Andersson, and G Backstrom, J. Phys. E: Sci. Instrum. **10**, 474 (1977).
[21] A. Grzybowski, M. Paluch, K. Grzybowska, and S. Haracz, J. Chem. Phys. **133**, 161101 (2010).
[22] W. Heinrich, B. Stoll, Progr. Colloid Polym. Sci. **78**, 37 (1988).

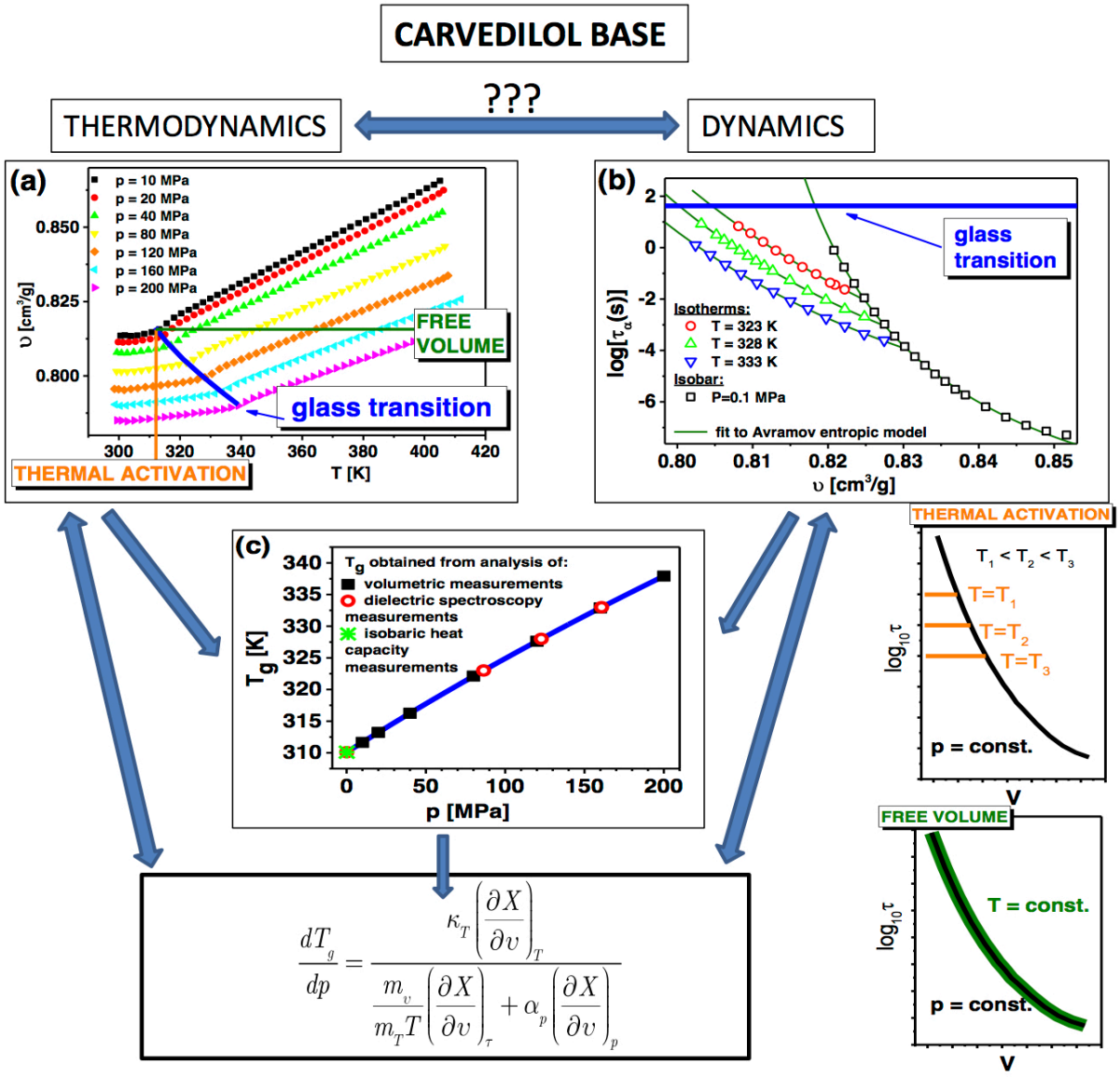
8.2. MATERIAŁY UZUPEŁNIAJĄCE ARTYKUŁ A4

1. UNIVERSAL EQUATION FOR THE PRESSURE COEFFIIENT OF THE GLASS TRANSITION TEMPERATURE IN THE CONTEXT OF DENSITY SCALING OF THE TOTAL SYSTEM ENTROPY

Very recently we have shown, that in the contrast to some results based on theoretical and simulations studies[1,2,3,4,5], τ_α is not in general a single variable function of total system entropy[6]. Nevertheless, it has to be noted that obtained result seems to be in accord with the newly reformulated theory of isomorphs[7,8]. Moreover, we have found that S can be scaled

versus $T\upsilon^{\gamma_S}$, where γ_S is only material dependent. Then, if the density scaling of structural relaxation times is fulfilled, we obtained that τ_α is a function of υ and S. Therefore in this paragraph we consider dT_g/dp in the context of the dependence $\tau_\alpha\left(\upsilon,S\right)$. In this case the complete differential of the structural relaxation time $d\tau_\alpha\left(\upsilon,S\right)$, at the glass transition defined at a constant value of τ_g, equals $0=d\tau_g\left(\upsilon,S\right)=\left(\frac{\partial\tau}{\partial\upsilon}\right)_S d\upsilon+\left(\frac{\partial\tau}{\partial S}\right)_\upsilon dS$. Since υ and S depend on T and p, one can rewrite last expression in the following form $0=\left(\frac{\partial\tau}{\partial\upsilon}\right)_S\left[\left(\frac{\partial\upsilon}{\partial T}\right)_p dT+\left(\frac{\partial\upsilon}{\partial p}\right)_T dp\right]+\left(\frac{\partial\tau}{\partial S}\right)_\upsilon\left[\left(\frac{\partial S}{\partial T}\right)_p dT+\left(\frac{\partial S}{\partial p}\right)_T dp\right]$. After regrouping and using Maxwell relations we obtain that $\frac{dT_g}{dp}=\frac{-\left[\left(\frac{\partial\tau}{\partial\upsilon}\right)_S\left(-\upsilon\kappa_T\right)+\left(\frac{\partial\tau}{\partial S}\right)_\upsilon\left(-\upsilon\alpha_p\right)\right]}{\left(\frac{\partial\tau}{\partial\upsilon}\right)_S\upsilon\alpha_p+\left(\frac{\partial\tau}{\partial S}\right)_\upsilon\frac{C_p}{T}}$. Since $\left(\frac{\partial\tau}{\partial S}\right)_\upsilon\left(\frac{\partial\upsilon}{\partial\tau}\right)_s\left(\frac{\partial S}{\partial\upsilon}\right)_\tau=-1$, the above equation transforms to $\frac{dT}{dp}=\frac{\left(\frac{\partial S}{\partial\upsilon}\right)_\tau\upsilon\kappa_T-\upsilon\alpha_p}{\left(\frac{\partial S}{\partial\upsilon}\right)_\tau\upsilon\alpha_p-\frac{C_p}{T}}$, where mentioned in the main text relation $\left(\frac{\partial S}{\partial\upsilon}\right)_\tau=\left(\frac{\partial S}{\partial\upsilon}\right)_T+\left(\frac{\partial S}{\partial T}\right)_\upsilon\left(\frac{\partial T}{\partial\upsilon}\right)_\tau$, can be used. Then, finally we obtain the equation identical with Eq. (4a) in the main text *i.e.,* with the equation received in the case of $\tau_\alpha\left(T,\upsilon\right)$. Similarly, if one considers $\tau_\alpha\left(p,S\right)$, the formula for dT_g/dp, which is the same as Eq. (4b) (and hence also as Eq. (4a)), could be obtained.

2. CONNECTION BETWEEN THERMODYNAMICS AND DYNAMICS RESULTS FROM UNIVERSAL EQUATION FOR THE PRESSURE COEFFICIENT OF THE GLASS TRANSITION TEMPERATURE



From the volumetric measurements (a) one can clearly see that the glass transition does not take place at constant volume or temperature, thus T_g depends on p. However, the glass transition line is in a perfect agreement with the isochronal conditions (c) established in dielectric spectroscopy experiment (b). Taking into account the definition of the glass transition temperature formulated on the assumption of the isochronal conditions we find a universal equation for dT_g / dp, which is independent on the thermodynamic quantities,

which changes reflect the glass formation, e.g., $X = v$ for the volumetric measurements or $X = S$ in the case of the calorimetery measurements. Moreover, our universal equation openly takes into account the roles of the temperature and the volume in the molecular dynamics, which is also reflected in the pure thermodynamic measurements, i.e., volumetric measurements. Therefore, our result fastens the thermodynamics and dynamics of supercooled liquid together, in simple way. Since, universal equation derived by us can describe the both limiting cases, i.e., "free volume" and "thermal activation", it clearly shows that dynamics of supercooled liquids is reflected in their thermodynamic in a such big way that none relation among the thermodynamic coefficients at the glass transition can be established, unless the additional restriction (or "feature" of the molecular dynamics) met at the glass transition would be found. Above conclusion opens new perspectives to the old standing open questions about the use of the equivalent to the Ehrenfest equations not only to the glass formation but also to any isochronal process.

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[1] Y. Rosenfeld, J. Phys. Cond. Matter **11**, 5415 (1999)
[2] M. J. Pont, J. R. Errington, T. M. Truskett, J. Chem. Phys. **134**, 081101 (2011).
[3] R. Chopra, T. M. Truskett, J. R. Errington, J. Chem. Phys. **133**, 104506 (2010).
[4] R. Chopra, T. M. Truskett, J. R. Errington, J. Phys. Chem. B **114**, 16487 (2010).
[5] G. Galliero, C. Boned, J. Fernandez, J. Chem. Phys. **134**, 064505 (2011).
[6] K. Grzybowska, A. Grzybowski, S. Pawlus, J. Pionteck, and M. Paluch, Phys. Rev. E **91**, 062305 (2015).
[7] L. Bohling, N. P. Bailey, T. B. Schrøder, and J. C. Dyre, J. Chem. Phys. **140**, 124510 (2014)
[8] T. B. Schrøder, and J. C. Dyre, J. Chem. Phys. **141**, 204502 (2014)